A STUDY OF ELECTROPHILIC ADDITION REACTIONS
TO
RUTHENIUM VINYLIDENE COMPLEXES

by

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To my loving parents, Timothy and Armyline Beach,

for their constant support and encouragement throughout this project.

Abstract

The electrophilic addition reactions of H^+ (from $HBF_4{\bullet}Et_2O$) and Me^+ (from MeOTf) to two series of Ru-vinylidene complexes, (1) $Cp^*RuCl(=C=CH(R))(PPh_3)$, (R = ^{t}Bu, **70a**; ^{n}Bu, **70b**; Ph, **70c**), and (2) $TpRuCl(=C=CH(R))(PPh_3)$, (R = ^{t}Bu, **74a**; ^{n}Bu, **74b**; Ph, **74c**), were investigated. These complexes were all observed to undergo electrophilic addition of H^+ to C_β of the vinylidene ligand through reaction with a 1.2 molar excess of $HBF_4{\bullet}Et_2O$ at $-78\,^\circ C$ to yield the new Ru-alkylidyne species $[Cp^*RuCl(\equiv C{-}CH_2(R))(PPh_3)][BF_4]$, (R = ^{t}Bu, **71a**; ^{n}Bu, **71b**; Ph, **71c**), and $[TpRuCl(\equiv C{-}CH_2(R))(PPh_3)][BF_4]$, (R = ^{t}Bu, **75a**; ^{n}Bu, **75b**; Ph, **75c**), respectively. Anion metathesis of **71a** and **71b** with $Na[B(Ar^f)_4]$ was also carried out through direct reaction at room temperature to yield the $B(Ar^f)_4$ salts $[Cp^*RuCl(\equiv C{-}CH_2(R))(PPh_3)][B(Ar^f)_4]$, (R = ^{t}Bu, **72a**; ^{n}Bu, **72b**). Structural characterization of **72a** by X-ray crystallography made possible the confident characterization of all remaining alkylidynes using ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Comparisons of spectral data and complex stability were also drawn between **71a-c** and **75a-c** with speculation as to the contributions of the steric and electronic properties of the ancillary ligands and alkylidyne substituents to these differences.

Reversal of these protonation reactions (*i.e.*, as revealed by NMR spectroscopic analysis) through treatment of the alkylidyne species with an appropriate Lewis base was also demonstrated for **71a**, using KO^tBu, and **71b**, using NEt_3 and PPh_3.

Conversely, the reaction of the aforementioned vinylidenes with MeOTf at room temperature did not result in the electrophilic addition of Me^+ to C_β of the vinylidene ligand, but rather the abstraction of the chloride ligand to form MeCl (identified by ^{1}H NMR spectroscopy). In the cases of complexes **70a** and **74a-c**, these reactions were sufficiently selective to allow the confident identification of the triflato(vinylidene) complexes $Cp^*Ru(OTf)(=C=CH(Ph))(PPh_3)$, **73c**, and $TpRu(OTf)(=C=CH(R))(PPh_3)$, (R = ^{t}Bu, **76a**; ^{n}Bu, **76b**; Ph, **76c**), respectively, using ^{1}H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectroscopy.

The application of **71a** to the alkyne cross metathesis of the 2-propynyl substrate $MeC{\equiv}CPh$ with itself was also explored. All attempts at this catalytic process failed despite the use of CuCl (*i.e.*, phosphine scavenger) and $AgBF_4$ (*i.e.*, chloride abstracting agent) as co-catalysts.

Acknowledgements

First and foremost, I would like to express my deepest gratitude and appreciation to my supervisor, Dr. G. J. Spivak who organized both my Honours and Masters research projects at Lakehead University. His constant guidance and encouragement was a generous contributor to my academic advancement over the past four years, and his consultations concerning my research progress never failed to further inspire me toward the achievement of laboratory goals.

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I would also like to thank Mr. K. Pringnitz for his assistance throughout my research project, primarily for instruction on the use of NMR spectroscopy but also for the combustion analyses of complexes **70b** and **72a**.

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Abbreviations

[M] = metal complex fragment

R/R' = alkyl or aryl group

RO = alkoxide or aryloxide group

Ar = aryl group

Me = methyl group, $-CH_3$

Et = ethyl group, $-CH_2CH_3$

Pr = propyl group, $-CH_2CH_2CH_3$

^{i}Pr = isopropyl group, $-CH(CH_3)_2$

^{t}Bu = *tert*-butyl group, $-C(CH_3)_3$

^{n}Bu = *n*-butyl group, $-CH_2CH_2CH_2CH_3$

Ph = phenyl group, $-C_6H_5$

Cy = cyclohexyl group, $-C_6H_{11}$

tol = $-(p\text{-}C_6H_4CH_3)$

Mes = mesityl group, −(2,4,6-trimethylphenyl)

Ts = tosyl group, −(4-toluenesulfonyl)

TBS = *tert*-butyldimethylsilyl group, $-Si(^tBu)Me_2$

Ar^f = $-(3,5\text{-}C_6H_3(CF_3)_2)$

Naph = 1-naphthyl group

NHC = "N-heterocyclic cabene"

PPh_3 = triphenylphosphine

PCy_3 = tricyclohexylphosphine

COD = 1,5-cyclooctadiene

COT = 1,3,5,7-cyclooctatetraene

p-cymene = 1-methyl-4-isopropylbenzene

Cp$^-$ = cyclopentadienyl anion

Cp^{*-} = 1,2,3,4,5-pentamethylcyclopentadienyl anion

dippe = 1,2-bis(diisopropylphosphino)ethane, $(^iPr)_2PCH_2CH_2P(^iPr)_2$

dppe = 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$

dfepe = 1,2-bis[bis(pentafluoroethyl)-phosphino]ethane, $(F_5C_2)_2PCH_2CH_2P(C_2F_5)_2$

Cyttp = $PhP(CH_2CH_2CH_2PCy_2)$

TPPMS = $Ph_2P\{2\text{-}OS(O)_2C_6H_4\}^-Na^+$

$^-OTf = {}^-OSO_2CF_3$

HOTf = triflic acid

Et_2O = diethyl ether, $O(CH_2CH_3)_2$

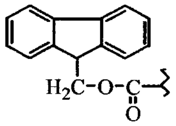
MeOH = methyl alcohol

EtOH = ethyl alcohol

^{i}PrOH = isopropyl alcohol

THF = tetrahydrofuran

Fmoc = (9-fluorenylmethyloxycarbonyl) group,



δ = chemical shift, ppm

ppm = parts per million

$^nJ_{AB}$ = NMR coupling constant between "A" and "B" through "n" covalent bonds, Hz

Hz = hertz, cycles per minute

dd = "doublet-of-doublets"

td = "triplet-of-doublets"

$\nu(A)$ = IR vibrational frequency, cm^{-1}

cm^{-1} = wavelengths per centimeter

Å = angstrom unit, 10^{-10} m

N/A = not applicable

Δ = heat added to reaction

RT = room temperature

atm = atmospheric pressure, 101.3 kPa

K = kelvin unit

equiv. = molar equivalent(s)

D = deuterium, ^{2}H

hrs. = time in hours

min. = time in minutes

λ_{max} = wavelength of maximum UV-Vis absorption, nm

nm = nanometers

HMQC = Heteronuclear Multiple Quantum Correlation

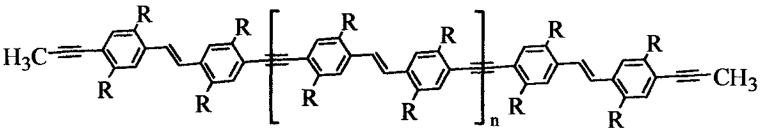
HMBC = Heteronuclear Multiple Bond Correlation

SM(A) = starting material of "**A**"

SM(A)' = starting material of "**SM(A)**" or alternate starting material of "**A**"

(A)* = synthetic intermediate in the preparation of "**A**"

PPVE = poly(*p*-phenyleneethynylene)/poly(*p*-phenylenevinylene) hybrids

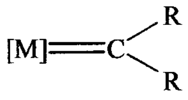


1. Introduction

In the field of organometallic chemistry, there has been emphasis in recent years on the development of processes which may be utilized to form carbon-carbon multiple bonds in accordance with specific synthetic purposes. Among the most significant of these are two known as *olefin metathesis* and *alkyne metathesis*. Over the last few decades, these synthetic techniques have established themselves as indispensable and unrivalled tools for the production of a cavalcade of otherwise costly and elusive target compounds. The undeniable success of these methods is, however, the result of the diligent development of suitable catalytic species which are essential to the progression of these metathetic reactions. While there have been some instances of olefin and alkyne metathesis reactions being effected by heterogeneous catalyst systems,[1] the ambiguity of the active catalytic species in these materials confounds their further improvement towards more active and process-selective agents. Thus, it is easy to understand why the vast majority of research carried out in catalyst design has dealt with homogeneous systems, especially since these are easily characterized using spectroscopic methods. This fashion of development ultimately generates the potential for tailoring of the catalyst design to suit ideally any application imaginable.

1.1 Olefin Metathesis Processes

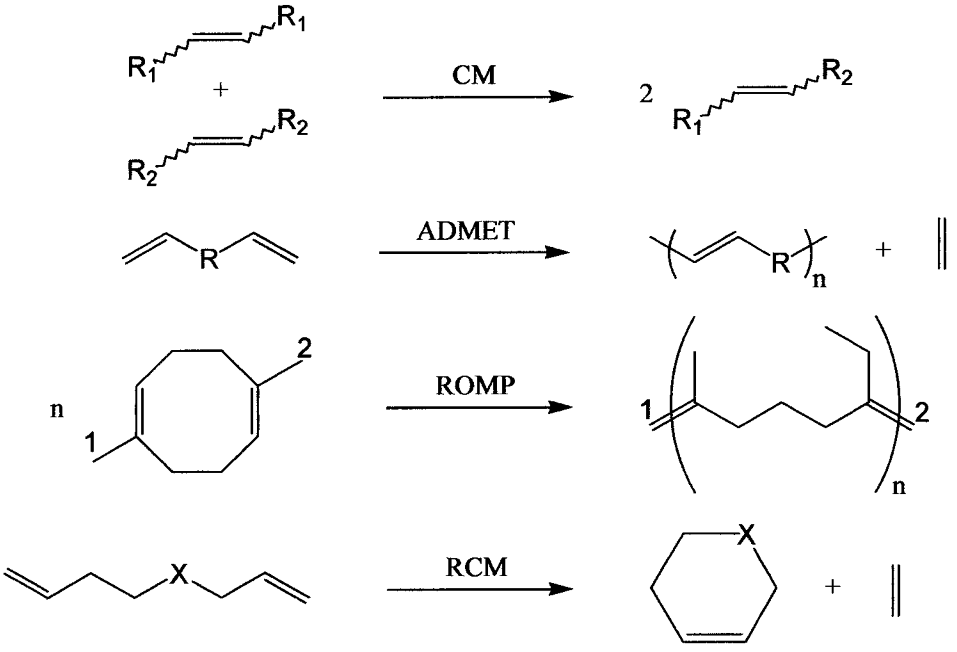
In *olefin metathesis*, which involves the rearrangement of alkene double bonds by appropriate catalyst species,[2a] the true molecular structure of the catalyst is well understood in most cases, with one functionality common to all compounds of this nature, this being an *alkylidene* ligand. These moeities are characterized as consisting of a carbon atom which is doubly bonded to the metal atom center of the complex (Figure 1). It is this trait which enables these *metal-alkylidenes* to fulfill their roles as catalysts for the metatheses of olefin substrates.



[M] = metal complex
R = alkyl or aryl group

Figure 1

Before thought may be given to the design and application of olefin metathesis catalysts, review of the various types of metatheses[2a] must first be undertaken (Scheme 1).



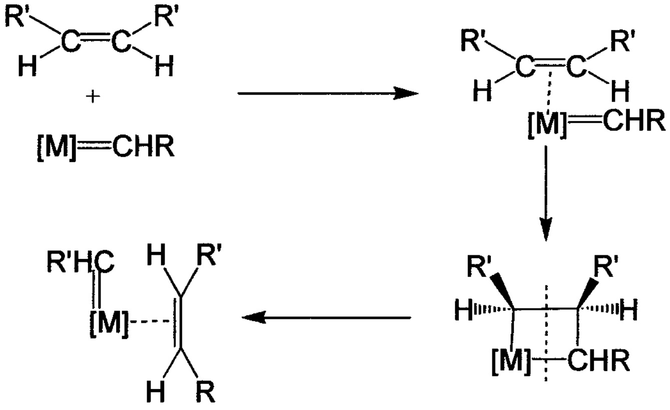
Scheme 1

Perhaps the simplest example of olefin metathesis is *cross metathesis* (CM).[2b] This process involves the simple interchanging of substituents between two different acyclic olefin molecules to form two identical olefins. Another acyclic olefin metathesis process involves the coupling of straight-chain diene substrates to form polymeric materials; as such, it is termed *acyclic diene metathesis polymerization* (ADMET). This process is complicated by its inherent thermodynamic unfavorability, but is driven forward by the production of ethylene (*i.e.* when terminal alkenes are used), which may be removed easily from the reaction mixture.

Taking the utilization of cyclic alkene substrates into consideration, there may be effected the opening of these ring species, with the inclusion of some other terminal alkene, to form a terminally substituted acyclic alkene through *ring-opening metathesis* (ROM). This process may also be applied to the formation of polymeric materials through a process known as *ring-opening metathesis polymerization* (ROMP). In either case, the driving factor for propagation of the reaction is the alleviation of the ring strain experienced by all cyclic alkenes.

Alternatively, the reverse of the ring-opening processes may be accomplished using *ring-closing metathesis* (RCM) which essentially serves to cross-metathesize a diene's double bonds with one another to form a cycloalkene. However, this process is understandably mediated by the extent of the ring strain generated as a result of formation of the cycloalkene (*i.e.* typically only useful in forming 5-membered and higher cycloalkenes), but at the same time may be facilitated by the evolution of ethylene.

Despite the superficial dissimilarities of these processes, there is currently a generally-accepted reaction mechanism common to all olefin metathesis processes that are catalyzed by a metal-alkylidene (Scheme 2). This mechanism, first proposed by Chauvin in 1970[2c], speculates that the first step of the metathesis process involves the coordination of the alkene substrate to the metal in a π-fashion. The resultant η^2-alkene complex then rearranges to form a metallacyclobutane intermediate. Cleavage of this intermediate yields the desired metathesis product as well as another molecule of catalyst. This mechanism has found support by the isolation of *metallacyclobutadiene* complexes by Schrock et al. in 1982 (*vide infra*).



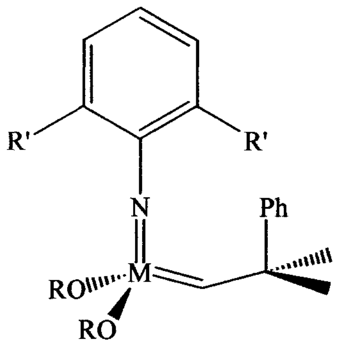
Scheme 2

In terms of effecting olefin metathesis, it should be noted that the first step of the accepted mechanism, which involves the coordination of an alkene molecule to the metal atom, requires a vacant site on the metal. This property highlights the fact that an effective catalyst complex should either possess a vacant coordination site on the metal, as is the case with Schrock-type complexes, or some labile ligand which may readily dissociate to generate a vacant metal site, as is the case with Grubbs-type complexes (*vide infra*).

1.2 Olefin Metathesis Catalyst Complexes

1.2.1 *Schrock-type Catalysts*

To date, the vast majority of metathesis processes have been carried out utilizing a wide variety of alkene substrates and metal-alkylidene catalysts. The first-developed class of these catalysts, often referred to as "Schrock-type", were introduced by Schrock in 1986[3a] and utilize early transition metal atoms as the coordination centre, typically Mo or W (Figure 2). The ancillary ligands of these compounds were specifically chosen and designed to have good σ- and/or π-donating properties (*e.g.* imido, alkoxide,[3d] aryloxide[3d]). This generous donation of electron density is indispensable in the application of these compounds to metathesis since the early metal atom centre is already relatively electron-deficient. This deficiency is also the principle reason that Schrock-type catalysts are best suited for metathesis of alkene substrates with alkyl or aryl substituents. Alternatively, substrates with heteroatom-containing substituents (*e.g.* alcohols, carbonyl groups, -NR_2) may result in the deactivation of the catalyst species through competitive coordination of these substituents to the highly electrophilic metal atom



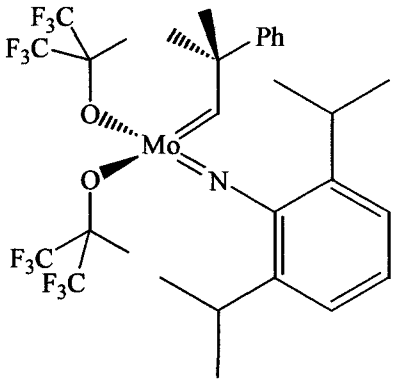
M = Mo, (W)
RO = alkoxide, aryloxide
R' = Me, ^{i}Pr

Figure 2

as opposed to the substrates' C-C double bonds.[4]

1.2.1.1 *Schrock-Type Metal-alkylidene Catalysts*

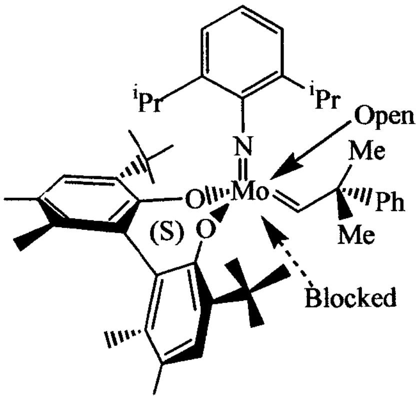
Despite this limitation in reactivity of Schrock-type complexes, the most widely used metal-alkylidene-based olefin metathesis catalyst is one first developed by Schrock et al. in 1990 (**1**).[5a] This compound, which has been commercially available for some time, is generally observed to be the "workhorse" of the metathesis catalyst market since it has proven itself as a highly-reactive and versatile species for this application.[5b,c]



1

1.2.1.2 *Asymmetric Alkene Metathesis Catalysts*

Similar to **1**, Schrock-type catalysts which incorporate large, chiral bidentate ligands have been developed which have displayed elaborate activity in asymmetric alkene metathesis (AAM). This area of stereoselective processes represents the next frontier in metathesis chemistry. Here, the progression of the metathesis reactions depends strongly upon the stereochemistry of the substrate molecules, thereby yielding optically enriched products. Two fine examples of effective AAM catalysts are the highly enantioselective (*S*)-Mo-biphenolate (**2**)[6] and (*R*)-Mo-binaphtholate (**3**)[7] complexes developed by Schrock et al.



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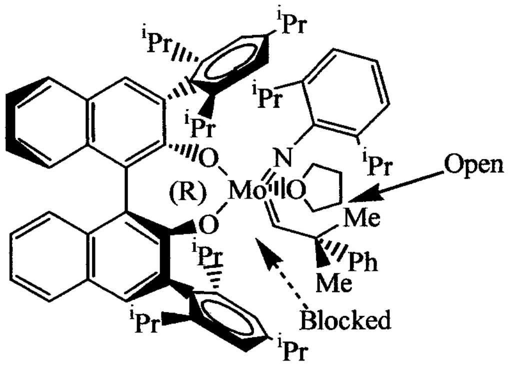
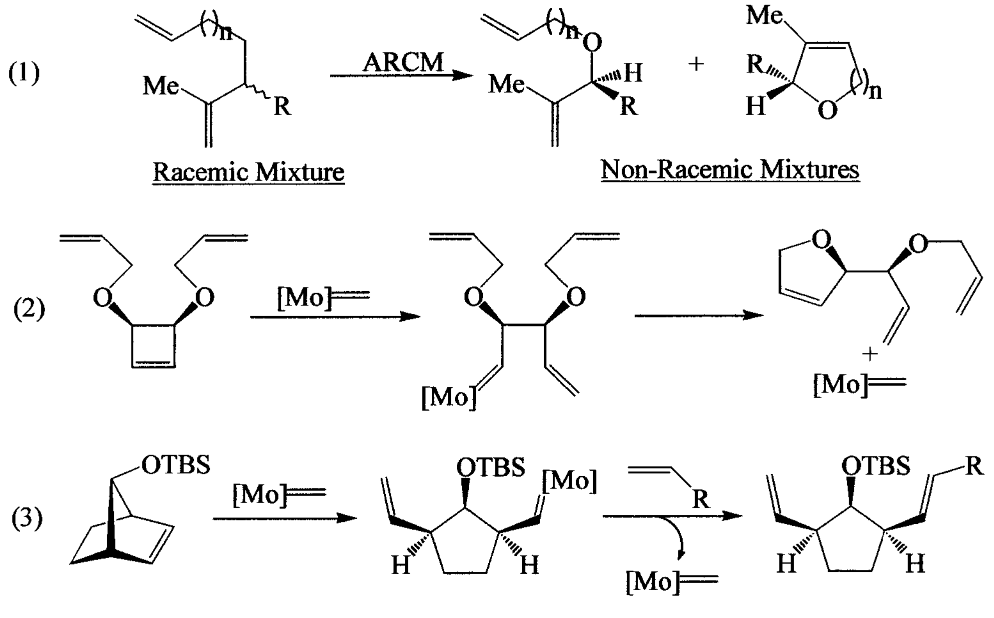


3

To date, the most investigated reactions in this field are asymmetric ring-closing metathesis (ARCM),[8a] asymmetric ring-opening/ring-closing metathesis (AROM/RCM),[8b] and asymmetric ring-opening/cross metathesis (AROM/CM)[8c] of which examples are given in Scheme 3.



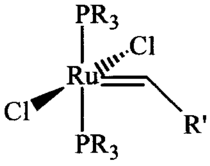
Scheme 3

In light of the observed diversity in application of Schrock-type metathesis catalysts, it is very easy to understand why they have held competitive positions in various synthetic processes.

With high reactivity, however, there often comes high instability, a condition from which these complexes are certainly not exempt. Their electron-deficient nature renders them particularly susceptible to nucleophilic attack by a variety of agents, especially water and oxygen.[8c] As a result, it is required that the reaction solvents be exhaustively dried and glove box techniques be used when utilizing these materials in synthetic procedures. Obviously, there is much to be improved upon in terms of stability for Schrock-type catalysts, at the very least, towards nucleophilic attack. The incorporation of late transition metals into catalyst design is one such improvement which has been diligently explored.

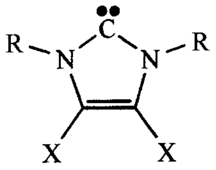
1.2.2 *Grubbs-type Catalysts*

The second class of olefin metathesis catalysts to emerge are known as "Grubbs-type" complexes. These complexes, which to date have been based mainly on the late transition metal Ru, have exhibited extraordinary activity towards the metathesis of hetero-functionalized olefin substrates ever since their introduction by Grubbs in 1992[9a] (Figure 3). Contrary to Schrock-type designs, the ligands of Grubbs-type complexes are not only strongly σ- and/or π-donating (*e.g.* halogens, phosphines,[9b] NHC-ligands), but may possess considerable π-accepting properties as well (*e.g.* most phosphines). Often referred to as "phosphine mimicks", *N-heterocyclic carbene* (*i.e.* NHC) ligands (Figure 4) simultaneously act as strongly σ-donating species and provide steric stabilization to the parent complex (see Section 1.2.2.2). All of the above ligands further serve to increase electron density on the already electron-rich Ru-atom, thereby increasing the metal atom's



R, R' = alkyl or aryl

Figure 3



R = alkyl, aryl, amine, ether, etc
X = alkyl, H, halide

Figure 4

binding preference for the olefin double bond as opposed to any heteroatoms on the functionalized olefin substrate.[4] A comparison of substrate compatibility of various alkylidene-supporting metals may be found in Table 1.[4]

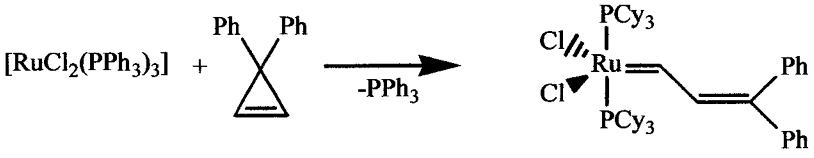
Table 1: Functional group tolerance of early and late transition metals

Tungsten	**Molybdenum**	**Ruthenium**	
Acids	Acids	**Olefins**	High Activity
Alcohols, water	Alcohols, water	Acids	
Aldehydes	Aldehydes	Alcohols, water	
Ketones	**Olefins**	Aldehydes	
Olefins	Ketones	Ketones	
Esters, Amides	Esters, Amides	Esters, Amides	Low Activity

The development of the first-generation of Grubbs-type catalysts has constituted perhaps the greatest innovation in olefin metathesis catalyst research. Each complex in this field adheres to the general formula $(PR_3)_2X_2Ru{=}CHR'$ ($X = -Cl, -Br, -OOCCF_3$) (*i.e.* similar to Figure 3 complex). They exhibit a much more robust stability toward both water and oxygen and as such are exceedingly easier to handle than Schrock-type complexes.[4]

1.2.2.1 *Grubbs-type Metal-alkylidene Catalysts*

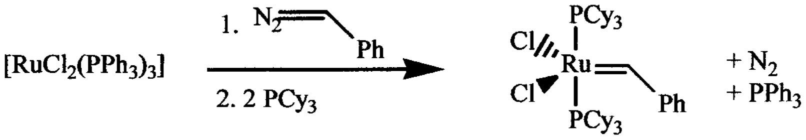
Initially, the methods for preparing these complexes were inconvenient. For instance, the seminal compound ($R{=}Cy$, $R' = -CH{=}CPh_2$, $X = -Cl$, **4**), while very active in RCM and ROM/CM processes,[5b] involves the isomerization of the highly unstable and hazardous diphenylcyclopropene by the Ru(II) centre of $RuCl_2(PPh_3)_3$[9] followed by simple phosphine exchange as outlined in Scheme 4.[10]



Scheme 4

4

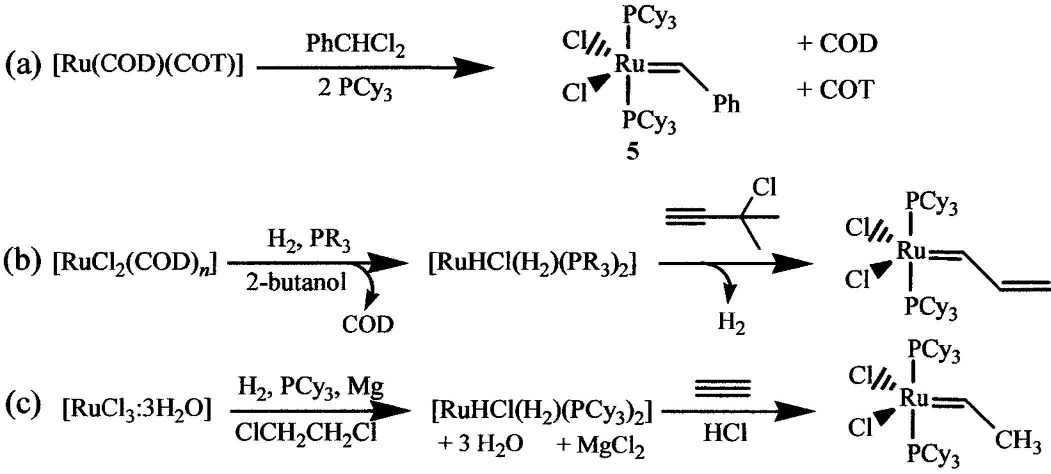
To improve upon this, Grubbs et al. began effecting the formation of carbene moieties through diazoalkene treatment of $RuCl_2(PPh_3)_3$, giving rise to the famous "Grubbs' catalyst", **5** (R=Cy, R'=CHPh, X= –Cl) (Scheme 5).[11]



5

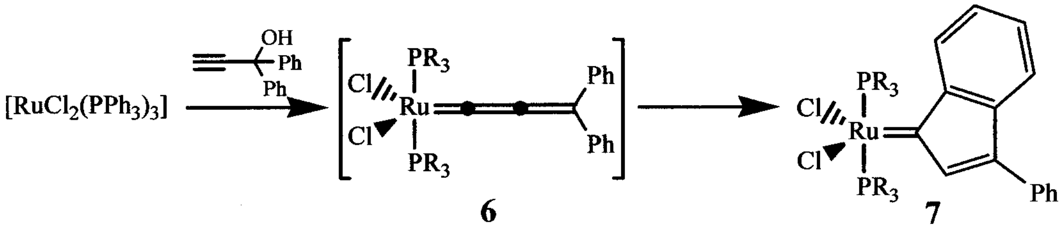
Scheme 5

Forgoing the use of these extremely hazardous reagents, Grubbs et al. in 1997 devised new vehicles for effective carbene formation using *gem*-dihalides (Scheme 6a)[12a] as well as propargyl chlorides (Scheme 6b).[12b] Later on, Werner et al. in 1998 introduced Ru-carbene formation using alkyne treatment of dihydrogen-hydridoruthenium complexes (Scheme 6c).[12c]



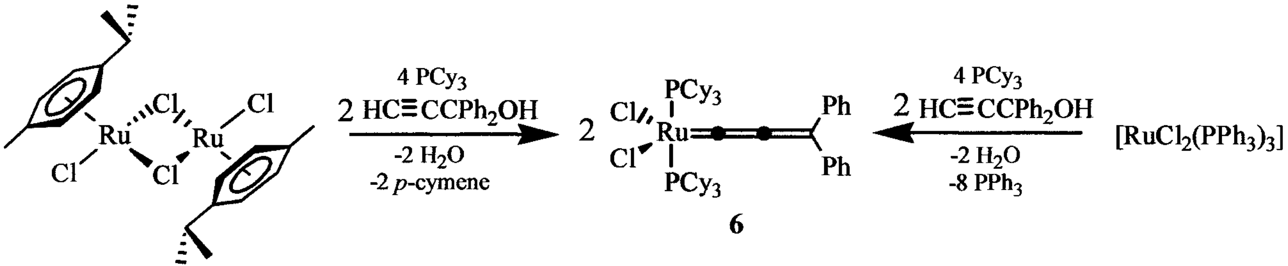
Scheme 6

Furthermore, Hill et al. attempted in 1999 to form the allenylidene $(PR_3)_2Cl_2Ru=C=C=CPh_2$, **6**, through simple treatment of $RuCl_2(PPh_3)_3$ with diphenyl propargyl alcohol.[13a] However, it was later revealed by Nolan et al. that the true structure of the product of this reaction is actually a phenylindenyl complex, **7** (Scheme 7).[13b]



Scheme 7

It wasn't until later that Nolan devised proper reaction conditions to facilitate the formation of the aforementioned allenylidene **6** (Scheme 8) which unfortunately, unlike **7** (perhaps more active in RCM than Grubbs' catalyst **5**[14]), is not significantly metathesis-active.[15]



Scheme 8

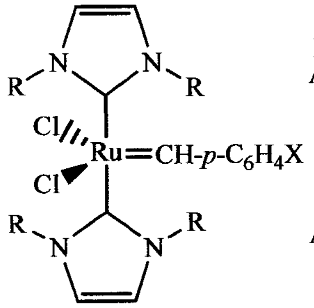
It should be noted at this time that each of the complexes mentioned above are thought to be precursors to the actual catalytic species. This is based on the observation that the first step of the most predominant olefin metathesis process is accepted as involving the dissociation of some ligand (*e.g.* PR_3) to yield a vacant coordination site on the metal *cis* to the carbene group, despite the uncertainty of whether this occurs before or after olefin coordination.[16, 26]

1.2.2.2 *N-Heterocyclic Carbene Ligands in Metal-alkylidene Catalyst Synthesis*

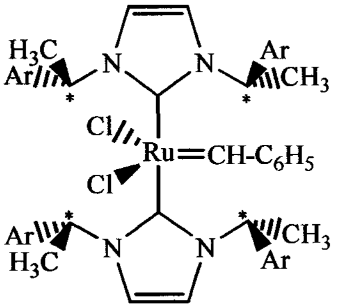
In terms of Grubbs' catalyst stability versus activity, the general trend observed is that these two attributes are inversely proportional to each other since a less stable catalyst will be able to dissociate a ligand more readily thereby facilitating effective metathesis, and vice versa. The challenge for synthetic chemists, therefore, is to devise some precursor species which readily decomposes to form the active catalyst, but is at that point stable enough to effect several catalytic cycles without decomposing completely. One way in which synthetic organometallic chemists have attempted (and achieved) this monumental structural adjustment is through the use of N-heterocyclic carbene (NHC) ligands (Figure 4).[17a]

Initially, it was thought that the strong σ-donation of NHC ligands coupled with their extreme steric demands[18] might serve to stabilize the reactive intermediates formed upon dissociation of some labile ligand at the beginning of the metathesis catalytic cycle. The main reason for this increased stabilization of the catalyst species when using NHC-ligands versus phosphines was postulated because the former are substantially stronger bases and are much more sterically demanding than trialkylphosphines.[17b-d] As a result, NHC-complexes are generally more thermally stable than their phosphine analogues, and as such, there may be a lower probability of continued complex decomposition following initial ligand dissociation.[17c]

In order to address this hypothesis, Herrmann et al. in 1998 began utilizing NHC ligands in metathesis catalyst synthesis with the synthesis of the seminal bis(carbene) complexes, **8**, in which both phosphines have been replaced with NHC ligands.[18]



8a: R = ^{i}Pr, X = H
8b: R = Cy, X = H
8c: R = ^{i}Pr, X = Cl

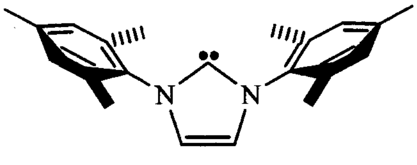


(*R*,*R*)-**8d**: Ar = Ph
(*R*,*R*)-**8e**: Ar = Naph

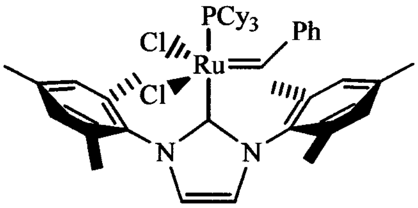
Complexes **8**, although structurally revolutionary, did not exhibit the increased reactivity in olefin metathesis that was expected to result from the use of these highly σ-donating ligands, despite the fact that **8a** was shown to be much more active in the ROMP of cyclooctene than Grubbs' catalyst **7**. In addition, **8b** was quite competitive with **8a** in the ROMP of cyclooctene as well as that of 2-norbornene. To match these complexes in metathesis activity, however, chiral complexes **8d** and **8e** required the higher temperatures at which **8a,b,d,** and **e** are equivalent in the RCM of 1,7-octadiene. Shortly after this work was published, three separate research groups in 1999, headed by Nolan, Grubbs, and Herrmann, almost simultaneously published manuscripts announcing the successful syntheses of complexes which incorporated both a phosphine ligand *and* an NHC ligand.

Nolan et al. synthesized perhaps the most logical representative of this second-generation of Grubbs-type catalyst through simple reaction of the famous **5** with the mesitylene-substituted carbene ligand, **9**,[19] to yield the heteroleptic complex, **10**.[19b] Several other analogous complexes with different R-groups on the carbene N-atoms have also been prepared by Herrmann et al.[20a] Soon after its introduction, **10** was shown to exhibit exceptionally high catalytic activity in the RCM of various diene substrates[20b] and in the ROMP of cyclic olefins,[20c] in most cases surpassing **5** in activity and yield. To further this work, Nolan et al. prepared the phenylindenyl complex, **11**, via a comparatively simpler route analogous to that of **7** with the addition of an NHC/phosphine exchange step.[21a] This complex is nearly equal to **10** in terms of activity toward RCM catalysis,[21b] and is a more favourable catalyst for olefin metatheses due to its relatively simple preparation.

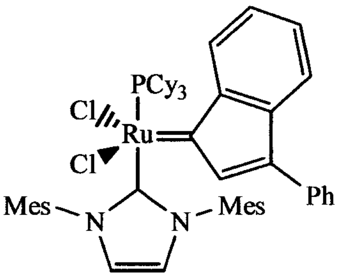
In an attempt to increase the reactivity of the metal fragment formed upon phosphine dissociation, Grubbs et al. incorporated saturated analogs of the aforementioned NHC ligands (**12**)[22] in the synthesis of the saturated NHC complexes, **13**.[21a] It was believed that the increased basicity of these saturated ligands[23b,c] would in turn increase the electron density on the metal, thereby yielding a more reactive catalyst.[23a,d] In actuality, **13** has effected the first example of formation of trisubstituted alkenes through intermolecular CM,[24] as well as the RCM and CM of electron-deficient alkenes.[25]



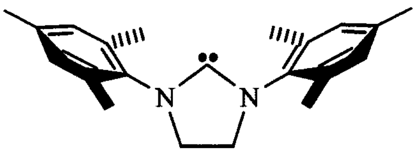
"IMes"
9



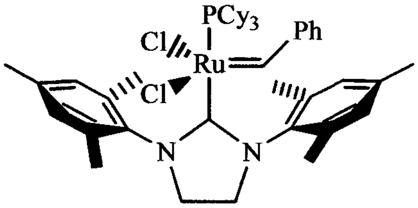
10



11

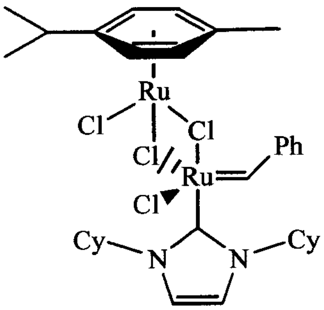


"SIMes"
12

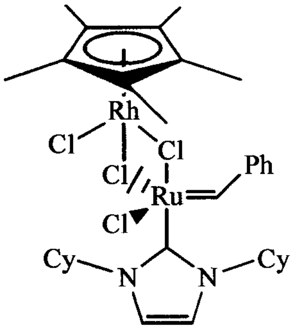


13

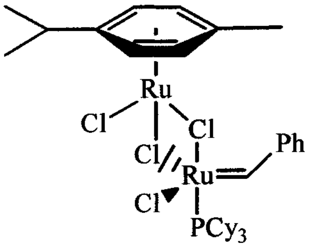
There have also been two bimetallic-NHC complexes, **14** and **15**, introduced by Herrmann et al., which are presumed to dissociate readily into their respective metal-fragment "ligands" through heterolytic cleavage of the chloro-bridges to form the active catalyst species (*i.e. dissociative* mechanism), a process which is driven forward by the dimerization of the subsequent metal fragments.[17d] This rationale is supported by relative ROMP rates of **14** and **15**[17d] compared to phosphine analogs, **16** and **17**, prepared by Grubbs et al., which likely follow an associative mechanism based on a near-linear dependence of some metathesis rates on substrate concentration.[26]



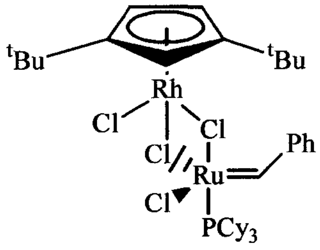
14



15

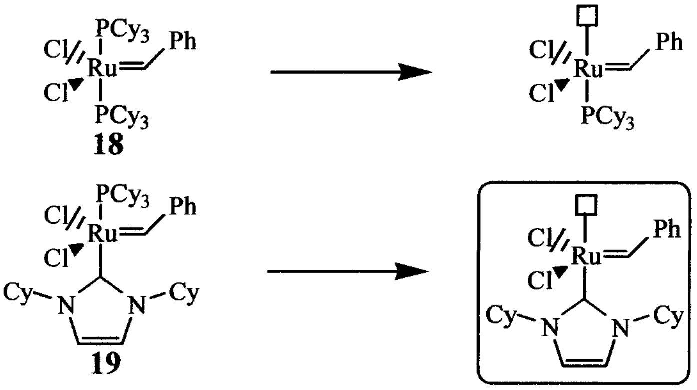


16



17

In any case, an increased basicity of the NHC ligand should subsequently increase the electron density on the metal. This attribute becomes particularly important when considering the relative activities of active catalyst species in first-generation versus second-generation Grubbs-type catalysts. For instance, comparative NMR experiments conducted by Herrmann et al.[17d] have indicated that the active catalyst species formed through phosphine dissociation from **18** is more active in the ROMP of 1,5-cyclooctadiene and cyclooctene than that formed from **19** (Scheme 9).

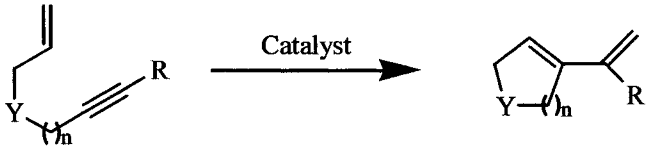


more active

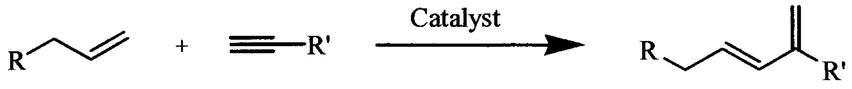
Scheme 9

1.2.2.3 *Grubbs-Type Alkylidenes in Enyne Metathesis*

The use of Grubbs-type alkylidenes in olefin metathesis has been well-documented, as was shown in the above sections. However, this utility extends in no small manner to substrates which contain C≡C bonds as well as C=C bonds. These substrates, termed *enynes*, may either be one molecule (*i.e.* metathesized "*intra*molecularly") or two molecules (*i.e.* metathesized "*inter*molecularly"), as Scheme 10 indicates.



Intramolecular Enyne Metathesis

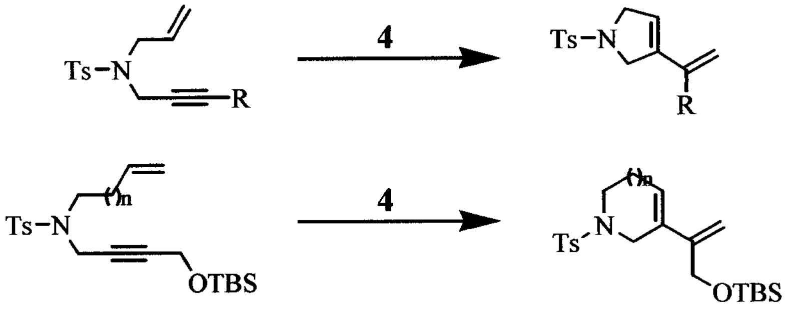


Intermolecular Enyne Metathesis

Scheme 10

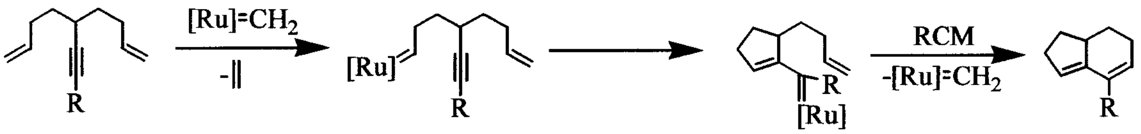
As for most types of olefin metathesis, the application range in *enyne metathesis* (EYM)[27a] is greatest for the "top-tier" Grubbs-type catalysts **4**, **5**, **10** and **13**. A brief overview of this area is given below.

The earliest example of EYM using a Ru-alkylidene is one reported by Mori and Kinoshita et al. in 1994[27b] which demonstrated the use of **4** in *ring-closing enyne metathesis* (RCEYM), an example of which is shown in Scheme 11.



Scheme 11

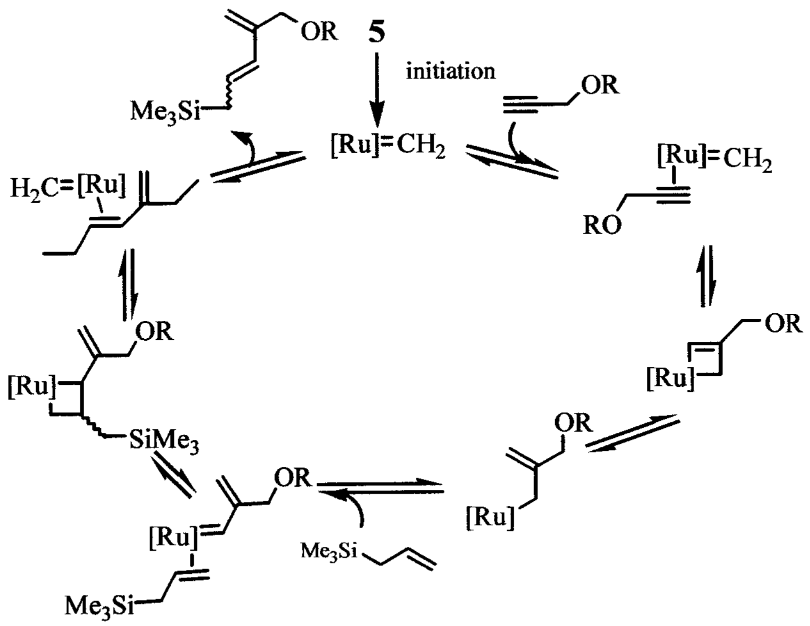
Later that year, Grubbs et al. reported the first use of tandem EYM in the formation of bicyclic systems, again with **4** as the precatalyst which is treated with ethylene prior to reaction to form the methylidene catalyst species[27c,d] (Scheme 12).



Scheme 12

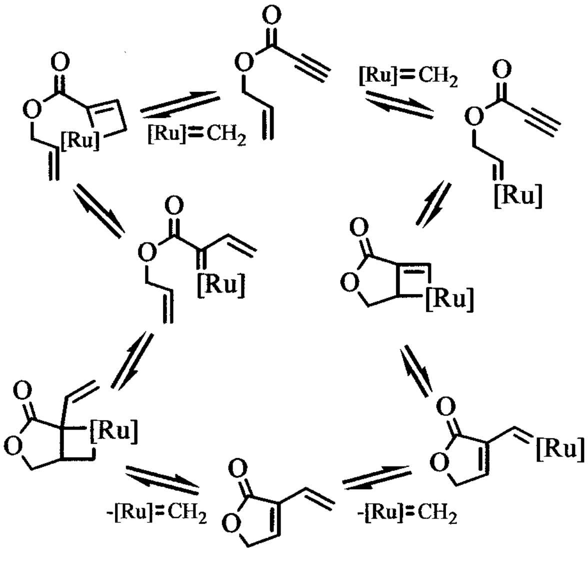
The 1998 report by Mori et al.[27e] displayed the virtue of ethylene use in the RCEYM of various internal substrates by **5**, while *cross enyne metathesis* (CEYM) activity of **5** was reported by Blechert et al. in 1997.[27f] Complexes **10** and **13** have also exhibited RCEYM activity toward a variety of enyne substrates.[27g-m]

In terms of the mechanism of enyne metatheses, there has been some speculation by two separate research groups in particular. For instance, during Blechert's report in 1997,[27f] there is a mechanism proposed for CEYM based on the NMR evidence that the alkyne substrates react with catalyst **5** faster than do the alkene substrates, but also that addition of alkene to the reaction mixture causes the alkynes to react rapidly. This led the authors to suggest that the alkyne is likely the first substrate to undergo metathesis followed by the alkene, as illustrated in Scheme 13.



Scheme 13

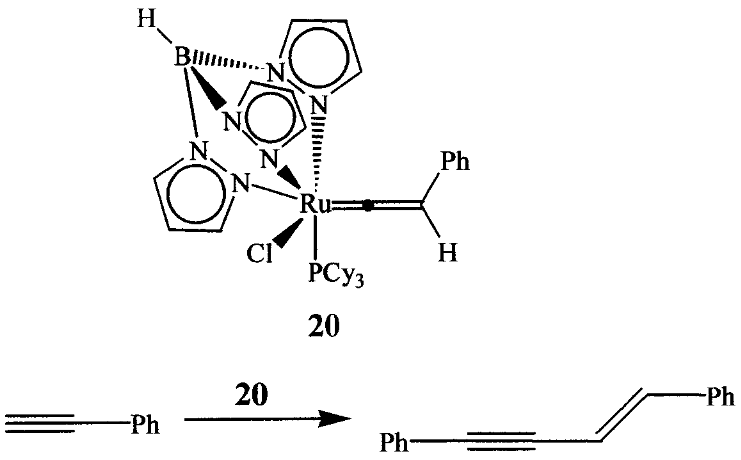
For RCEYM, similar studies conducted by Hoye et al. in 1999[27n] provided two potential pathways through which this process may occur using **5** as a catalyst: one which favours the first reaction of the alkyne, and the other of the alkene (Scheme 14). Once again, NMR analysis aided the elucidation of the "alkene-first" pathway as the preferred mechanism.



Scheme 14

1.2.2.4 *Grubbs-type Vinylidenes in Olefin Metathesis*

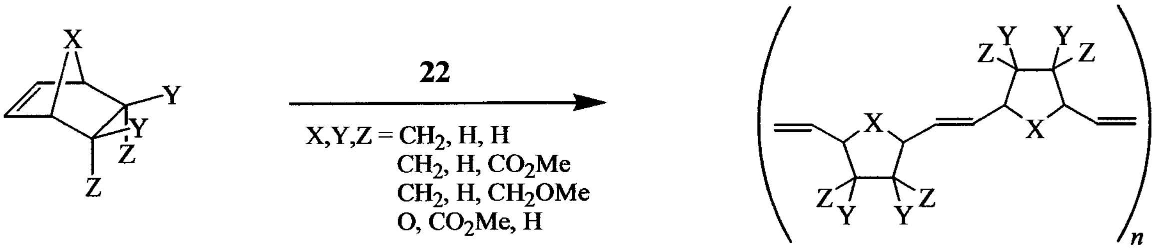
In addition to the systems described above, there have also been synthesized a few *Ru-vinylidene* compounds, which are able to catalyze alkene rearrangements, including metathesis. Prior to discovery of any metathesis-active Ru-vinylidenes, complex **20** has been shown to efficiently dimerize phenylacetylene to quantitatively form (*E*)-1,4-diphenyl-1-butene-3-yne (with ~5% of (*Z*) isomer),[28] as illustrated in Scheme 15.



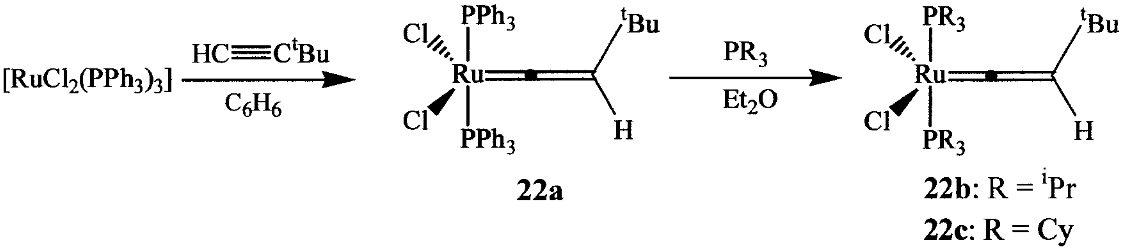
Scheme 15

Grubbs et al. were the first to demonstrate Ru-vinylidene-catalyzed ROMP of norbornene using the non-substituted complex $(PCy_3)_2Cl_2Ru{=}C{=}CH_2$, **21**,[29] although no concrete data concerning these experiments was provided upon publication. Furthermore, **21** is only accessible via the bubbling of propadiene into a solution of Grubbs'-catalyst **5** at −20°C.

The ROMP of norbornene derivatives, as outlined in Scheme 16, has also been achieved by Ozawa et al.[31] through the use of the Ru-vinylidenes $(PR_3)_2Cl_2Ru{=}C{=}CH({}^tBu)$ (R= Ph[30] (**22a**), ^{i}Pr[31] (**22b**), Cy[31] (**22c**)), with the PCy_3-substituted complex being the most active in this capacity. An obvious advantage of complexes **22** is that they are exceedingly easy to prepare. For example, complex **22a** is accessible through stirring $RuCl_2(PPh_3)_3$ with $HC{\equiv}C^tBu$ in benzene for 24 hours at room temperature, and may easily be followed by appropriate phosphine exchange in Et_2O (Scheme 17).

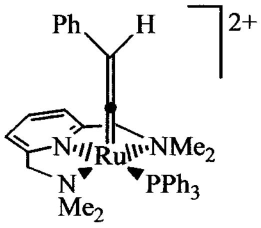


Scheme 16



Scheme 17

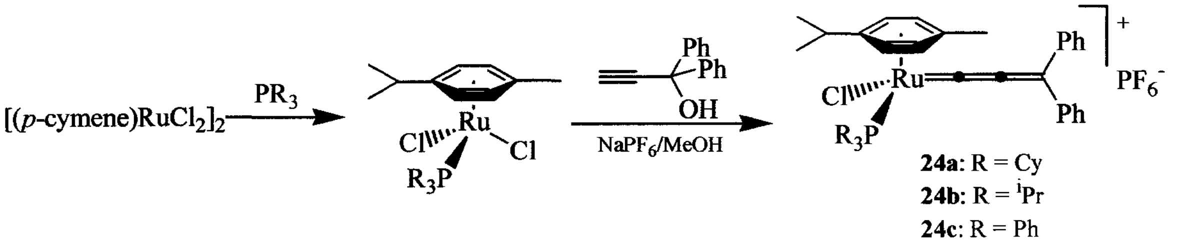
A dicationic Ru-vinylidene complex developed by van Koten et al. has also exhibited ROMP activity using norbornene as the substrate.[32] This complex, **23**, which contains the tridentate chelating ligand 2,6-bis[(dimethylamino)methyl]pyridine (*i.e.* "NN'N"),[33] is readily prepared using one equivalent of $AgBF_4$ to abstract a chloride from $RuCl_2(NN'N)(PPh_3)$ in the presence of excess $HC{\equiv}CPh$ in CH_2Cl_2, then one further equivalent to abstract another chloride and generate the coordinatively unsaturated complex. Coordinatively saturated analogs of **23** have not been found to be metathesis-active.



23

1.2.2.5 *Grubbs-type Allenylidenes in Olefin Metathesis*

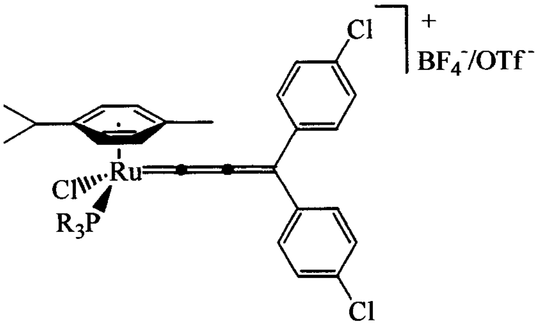
Contributions by Dixneuf, as well as Fürstner et al., to the field of cumulenylidene-based olefin metathesis catalysts have yielded a series of metathesis-active *Ru-allenylidene* complexes which are useful in the RCM of a multitude of functionalized dienes and even some eneynes. The first representatives of these species, introduced in 1998,[34a] feature η^6-*p*-cymene, diphenyl(allenylidene), and trialkylphosphine ligands, **24**. Cationic complexes **24**, in particular the PCy_3-substituted version, have found application in the RCM of a vast array of diene[34a] and eneyne substrates.[35] Preparation of **24** is effected simply by stirring the appropriate dichlorophosphino precursors (R= Cy (**24a**), ^{i}Pr (**24b**), Ph (**24c**))[34b,c] in MeOH at ambient temperature in the presence of $NaPF_6$ and excess diphenyl propargyl alcohol, an obvious synthetic advantage (Scheme18). Furthermore, the dependence of RCM activity of **24a** on the identity of the



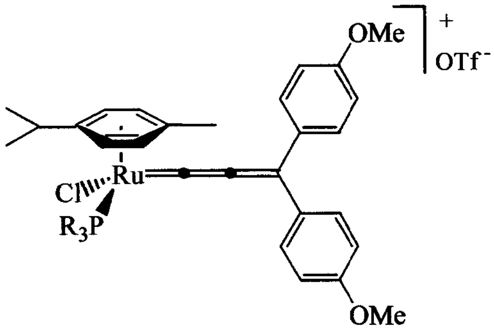
Scheme 18

escorting counterion has been illustrated through comparative studies.[36] The active catalytic species is thought to be stabilized by a weakly-coordinating counterion, such as OTf^-, and, as a result, is able to complete more catalytic cycles than if a non-coordinating ion were used (*e.g.* BF_4^-). This theory is supported by the greater observed RCM activity of **24a**•OTf^- compared to **24a**•BF_4^-.

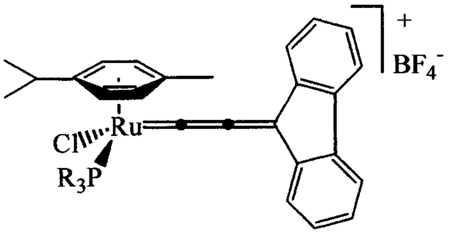
Analogous to **24** is another group of Ru-allenylidenes which have been shown to effect RCM of *N,N*-diallyltosyl amide, albeit with poor selectivity.[37] These complexes, **25**, are also conveniently obtainable from treatment of (*p*-cymene)$RuCl_2(PCy_3)$ at ambient temperatures in the presence of AgX (X = BF_4^-, PF_6^-, OTf^-) and an excess of the appropriate propargyl alcohol using aprotic solvents. In each case, the by-product species resulting from the initial metathesis reaction involving the allenylidene moiety of **25** and the olefin substrate is not observed, suggesting a dissimilarity in the mechanisms of



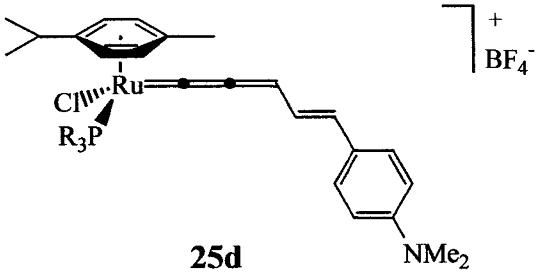
25a



25b



25c

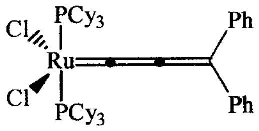


25d

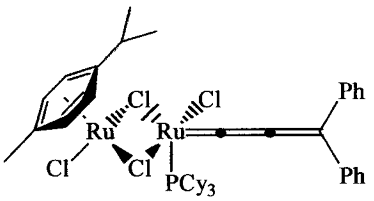
metathesis processes catalysed by Ru-carbenes as compared to these Ru-allenylidenes.

Based on the proposed decomplexation of *p*-cymene in the photoactivation of (*p*-cymene)$RuCl_2(PCy_3)$ toward olefin metathesis,[38] the initiation of complexes **24** and **25** via irradiation with UV light is thought to involve a similar pathway. This is supported by the fact that addition of excess *p*-cymene to catalytic mixtures of these complexes actually curtails metathesis activity. The same is true for addition of PCy_3, indicating a cooperation of these two dissociative mechanisms during metathesis. As a result, the use of coordinating counterions may accelerate metathesis possibly due to the fact that they would serve to stabilize the coordinatively unsaturated intermediates formed during the above processes.

Similar to Grubbs'-catalyst **5**, Hill et al. have synthesized two coordinatively unsaturated allenylidene complexes, **26** and **27**.[39] The preparation of **26** is achieved through simple addition of excess $HC{\equiv}CCPh_2OH$ to $RuCl_2(PPh_3)_3$ in refluxing THF, while **27** is obtainable from reaction of **26** with (*p*-cymene)$RuCl_2(PCy_3)$ at ambient temperatures. Soon after their introduction, Hill et al. illustrated that both **26** and **27** were capable of performing RCM on a variety of ***α,ω***-diene and dienyne substrates, with **26** exhibiting slightly higher activity.[39b]



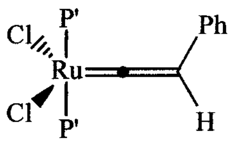
26



27

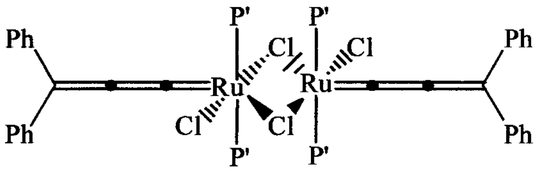
1.2.2.6 *Water-Soluble Grubbs-type Vinylidenes and Allenylidenes in Olefin Metathesis*

Work done by Romerosa et al. has produced the novel water-soluble vinylidene, **28**, and allenylidene, **29**, which have each been shown to effect the ROM of cyclopentene using methyl acrylate as the chain transfer agent. Complexes **28** and **29** are both obtainable from the common precursor complex $[\{RuCl_2(TPPMS)_2\}Na_2]_2\cdot 4H_2O$[40] (TPPMS = $Ph_2P\{2\text{-}OS(O)_2C_6H_4\}^-Na^+$) through reaction with equimolar HC≡CPh or $HC{\equiv}CCPh_2OH$, respectively, in MeOH, followed by a simple acetone/hexanes precipitation workup.[41] The main difference between these two complexes is that **29** tends to dimerize after preparation. While **28** is only ROM-active in homogenous MeOH reaction media, **29** is capable of operating in biphasic water/Et_2O mixtures. However, both agents require the presence of $HBF_4\cdot Et_2O$ in order to initiate metathesis.



28

P' = TPPMS



29

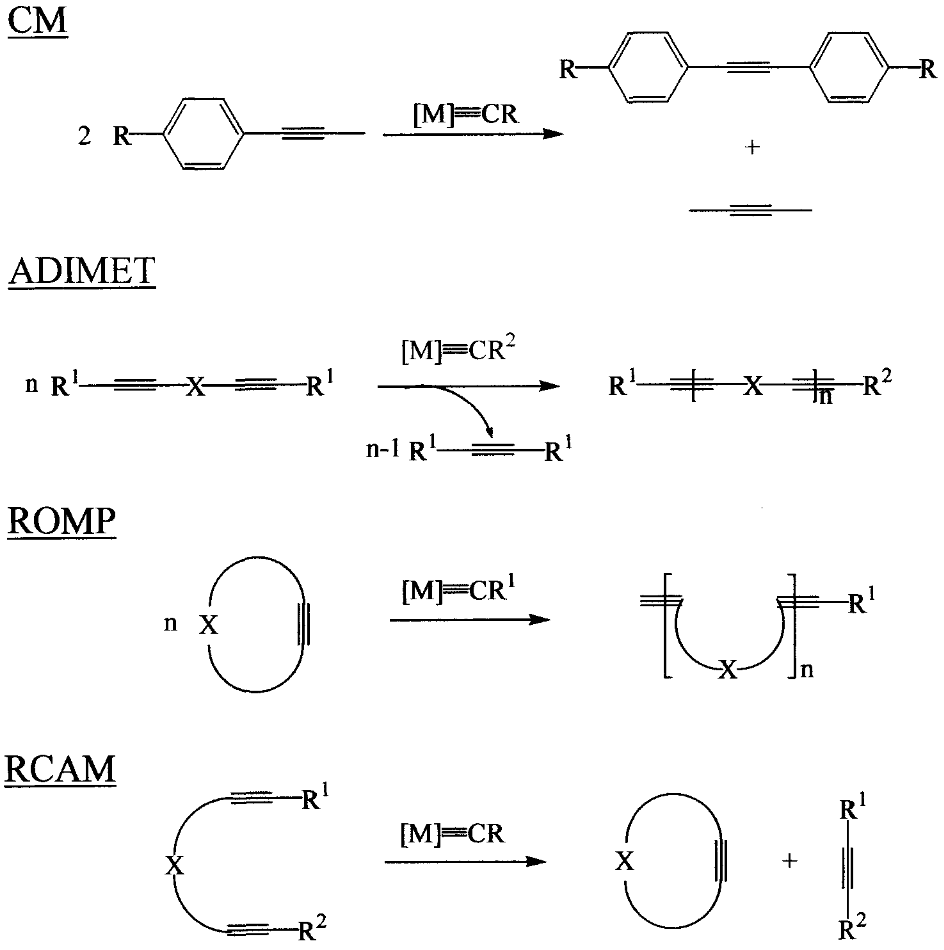
Given the apparent synthetic advantages of utilizing olefin metathesis, both in the convenience of implementation and diversity of application, it is logical to envision similar benefits arising from the use of analogous processes to effect transformations in alkyne substrates. Also, knowing the enormous utility of Ru-based systems in the metathesis of functionalized olefins, it is reasonable to hypothesize that the same may be true for Ru-based alkyne metathesis catalysts, despite the fact that no examples of these have yet been reported.

1.3 Alkyne Metathesis Processes

Analogous to the rearrangement of alkene substrates through *alkene metathesis*, there have also been developed several methods for effecting similar transformations of *alkyne* substrates known collectively as *alkyne metathesis*,[42] all of which are illustrated in Scheme19. In much the same way that alkene metatheses require the involvement of catalyst species, the corresponding alkyne processes are dependent on *metal-alkylidynes* in order to proceed effectively. These compounds include the essential *alkylidyne* moeity, which consists of a carbon atom triply bonded to the metal atom centre of the complex. Even in cases where non-alkylidene complexes are used as catalysts, it is believed that there may be a metal-alkylidyne intermediate involved in the catalytic cycle.[43]

The alkyne metathesis reaction is generally accepted as involving the interchanging of substituents between two alkyne molecules to form two new alkynes. This process, termed alkyne *cross metathesis* (CM), was the first observed form of alkyne metathesis and was first demonstrated by Mortreux et al. in 1974.[42] To avoid situations of product equilibrium, it is often arranged that the initial alkyne substrate is methyl-substituted. This way, the metathesis process results in the production of 2-butyne, a volatile compound which may be removed from the reaction mixture through the use of N_2 streams and higher reaction temperatures.[44] This serves to drive the reaction towards productive metathesis processes, thereby resulting in higher yields of desired products.

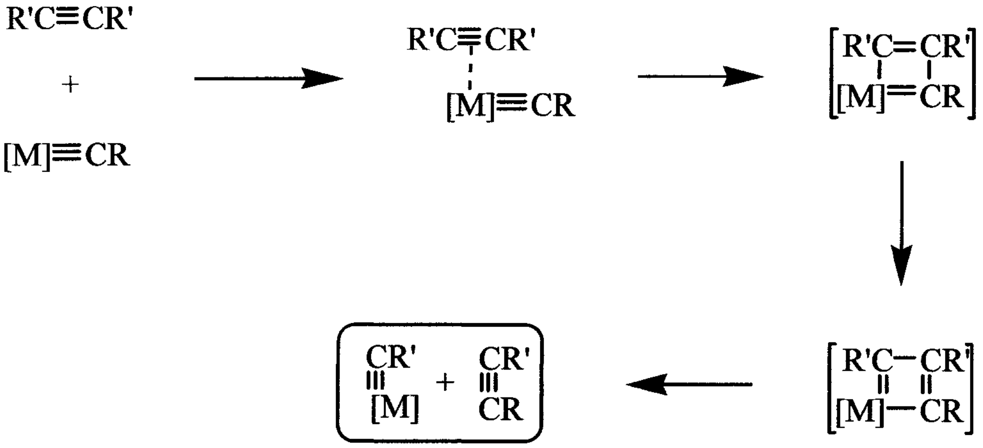
In 1987, Schrock et al. first demonstrated an alkyne metathesis process which forms polymeric materials from cycloalkyne starting materials. This *ring-opening metathesis polymerization* (ROMP)[45a] technique, like it's olefin-based sister process (see Section 1.1), takes advantage of the thermodynamically unfavourable ring strain associated with cyclic alkyne compounds and utilizes the alleviation of this strain as the driving force for polymer production.[45b] A similar process, known as *acyclic diyne metathesis* (ADIMET),[46] makes use of diyne substrates in the production of polymers. Once again, this metathesis process is effectively driven forward by the use of terminally methyl-substituted diynes with subsequent elimination of 2-butyne from the reaction mixture.



Scheme 19

Contrary to the aforementioned ring-opening alkyne processes, there has recently been introduced a method of producing cyclic alkyne molecules from acyclic diyne substrate materials. Appropriately referred to as *ring-closing alkyne metathesis* (RCAM),[47] this type of reaction also benefits from the use of terminally-methylated diyne substrates. As in previous metathesis methods, the productive metathesis of these substrates produces 2-butyne, the removal of which drives the reaction to completion. This is especially important when considering RCAM from a thermodynamic standpoint since the formation of cyclic alkynes creates unfavourable ring strain.[45b] It is also necessary to carry out RCAM processes under highly dilute reaction conditions in order to disfavour the onset of ADIMET side reactions.

Because of their dependance on catalysts, methodological considerations associated with the application of alkyne metathesis practices must take into account the currently accepted mechanism inherent of all alkyne metatheses, which is illustrated in Scheme 20. This mechanism, first postulated by Katz et al. in 1975,[48] is very similar to that of alkene metathesis (see Section 1.1). The first, and presumed rate-determining,[49] step of this mechanism is the π-coordination of an alkyne substrate molecule to the metal atom of the alkylidyne complex. The rearrangement of the subsequent η^2-alkyne species yields a metallacyclobutadiene intermediate. Rearrangement and cleavage of this species results in production of a new alkyne molecule and generation of another alkylidyne complex.



Scheme 20

Certainly the species which best supports the above mechanism of alkyne metathesis reactions is the metallacyclobutadiene intermediate, which is widely regarded as the "smoking gun" of both alkene and alkyne metathesis processes. Support for this species' pseudonym was provided by the isolation of the metallacyclobutadiene complexes $L_3W(C_3R_3)$ (L_3 = $[OC(Me_2)C(Me_2)O](O^tBu)$, Cl_3; R = Me, Et, ^tBu) by Schrock *et al.* in 1982[50] through reaction of alkylidyne complexes with acetylenes. Since the existence of these species has been proven to occur under conditions similar to those of alkyne metathesis, the above proposed mechanisms of alkene and alkyne metathesis are, therefore, very likely to be accurate.

As mentioned before, the effecting of alkyne metathesis requires the assistance of a suitable catalyst species, a point which is made abundantly clear upon examination of Scheme 15. A suitable catalyst species would ideally possess a reasonably balanced compromise between metathesis activity and compound stability. While several catalysts of this function include a fully-characterized alkylidyne moeity in their inherent structure, some do not, although there are suspected to be transient alkylidyne species involved in their catalytic cycles.[43]

1.4 Metal-Alkylidyne Complexes

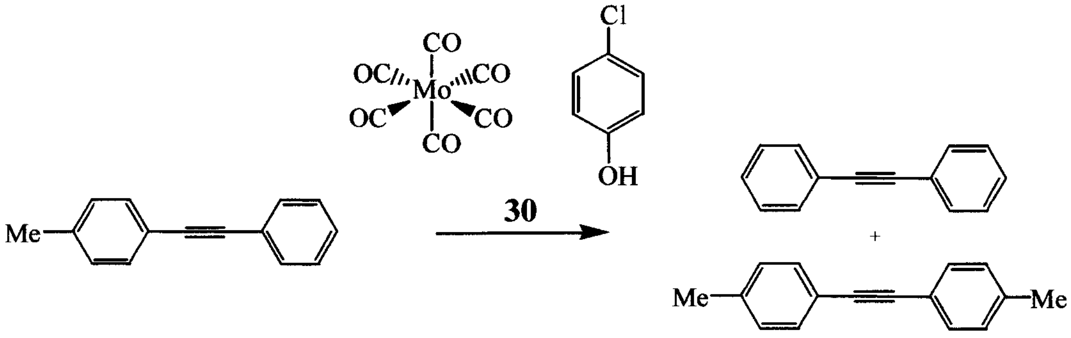
Over the past few decades, the scope of metal-carbon multiple bond research has focussed mainly on metal-alkylidenes, as alluded to in Section 1.2. However, development of related metal-alkylidyne species has also been steadily undertaken, providing many examples of M≡C bond moieties involving Group V, VI and VII metals[51a,b] as well as many with Os as the metal atom center.[51c-j] Despite this vast stockpile of alkylidyne complexes, only a select few have found use in the catalysis of alkyne metathesis processes.

1.4.1 *Alkyne Metathesis-Active Alkylidynes/Precursors*

Unlike olefin metathesis, alkyne metathesis does not possess the luxury of having a wide variety of effective catalyst compounds available for every desired application. In fact, there are comparatively few homogeneous systems that have thus far been established as consistently dependable catalysts for alkyne metathesis.

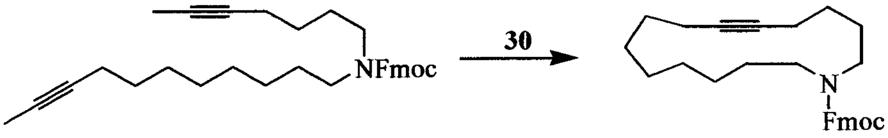
1.4.1.1 *Mortreux's Catalyst: $Mo(CO)_6/p\text{-}R\text{-}C_6H_4OH$*

The first example of alkyne metathesis made use of the poorly-defined homogeneous catalyst system one equiv. $[Mo(CO)_6]$/~ten equiv. [*p*-Cl-C_6H_4OH], **30**, in the CM of *p*-tolylphenylacetylene as depicted in Scheme 21.[42] Other examples of CM using **30** have also been reported.[52]



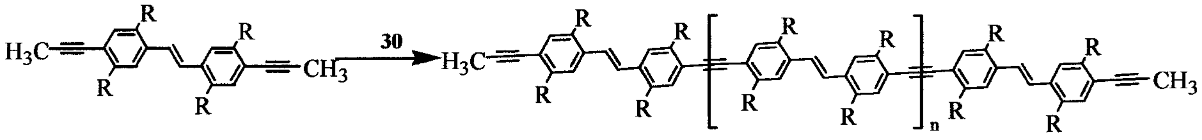
Scheme 21

Since its inception, **30** has also found application in RCAM processes.[53] The first example of this utility was demonstrated by Fürstner et al. in 1999.[53a] One special application of **30**, as illustrated in Scheme 22, is in the RCAM formation of the macrocyclic backbone of the cytotoxic marine alkaloid motuporamine C, which is has exhibited anticancer activity *in vitro*.[53d,e]



Scheme 22

Some research has also been carried out utilizing **30** in the facilitation of ADIMET processes. For instance, Bunz et al. demonstrated the use of $Mo(CO)_6$ with p-CF_3-C_6H_4OH to produce poly(p-phenyleneethynylene) (PPE) materials from p-dipropynylated benzenes using higher reaction temperatures.[43a] Another study by this group, as Scheme 23 illustrates, showcases the preparation of alkyl-substituted poly(p-phenyleneethynylene)/poly(p-phenylenevinylene) hybrids (PPVE) using **30** as the catalyst (R = Cl), a process which was effected with very good product yields (78-98%).[54]



R =3,7-dimethyloctyl, 2-ethylhexyl, dodecyl, octyl

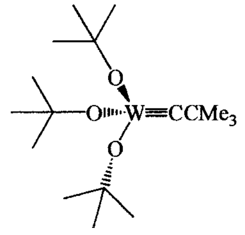
Scheme 23

In many alkyne metathesis reactions using **30**, the product yields obtained are typically fair to moderate (usually ~75% or lower).[43c, 52, 53] To improve upon these results some groups have adopted the convention of utilizing 2-propynyl species as substrates for these reactions,[55] which are then carried out at higher temperatures (e.g. in refluxing o-dichlorobenzene, ~150 °C). The metathesis of these species generates the volatile compound 2-butyne, which may be removed from the high-temperature reaction mixture using N_2 streams, often resulting in much higher product yields.[43a, 44]

Although **30** exhibits good catalytic activity in several applications, its real advantage lies in its convenience of preparation, using off-the-shelf reagents and solvents (i.e. no need for strict drying and degassing procedures, just N_2 atmosphere). Unfortunately, there has always been an air of ambiguity surrounding the true identity of the active catalytic species. This makes it difficult for synthetic chemists to determine proper courses of action for the improvement of catalytic activity and selectivity. Considering the fact that **30** exhibits it's best performance at high reaction temperatures (~150 °C), these improvements would perhaps be the most beneficial in extending the repertoire of compatible substrates to include those which may be more thermally stable.[53a,d] Since unambiguous identification of the active catalyst species in **30**, although long overdue, is not likely to occur in the immediate future, attention must be turned toward catalyst species which are more easily characterized. However, work done by Schrock et al. indicates that there may be metal-alkylidyne and metallacyclobutadiene intermediates involved in the catalytic cycle of **30**. This conclusion was based on the efficient exchange of various Mo-alkylidynes' substituents with those of added disubstituted alkynes (*i.e.* "stoichiometric metathesis") and the supposed formation of molybdacyclobutadienes due to data acquired through these studies which was analogous to that of similar tungstenacyclobutadienes.[56]

1.4.1.2 *Schrock's W-Alkylidyne Catalyst:* $({}^tBuO)_3W{\equiv}C^tBu$

Compelled by desires both to understand better the mechanism of alkyne metathesis and to improve the activity and selectivity of catalytic systems, Schrock et al. introduced, in 1981, a class of alkylidyne compounds which utilize W(VI) as the metal atom centre.[57] By far the most active member of this class in the field of alkyne metathesis is the widely-used W-neopentylidyne complex $({}^tBuO)_3W{\equiv}C^tBu$, **31**.[57a] This complex has gained the well-earned titles of both pioneer and workhorse of well-defined metal-alkylidyne-based catalysts for alkyne metathesis, being active in CM[57a] as well as effecting the first instances of ADIMET[46] and RCAM.[47] Examples of these processes may be found in Scheme 24. Due to its high reactivity with internal acetylenes, however, **31** is not suitable for use in ROMP reactions since it is expected to react with the triple bonds of the growing polymer chain.[45a] Complex **31**, like **30**, has also found utility in the preparation of motuporamine C[53d]



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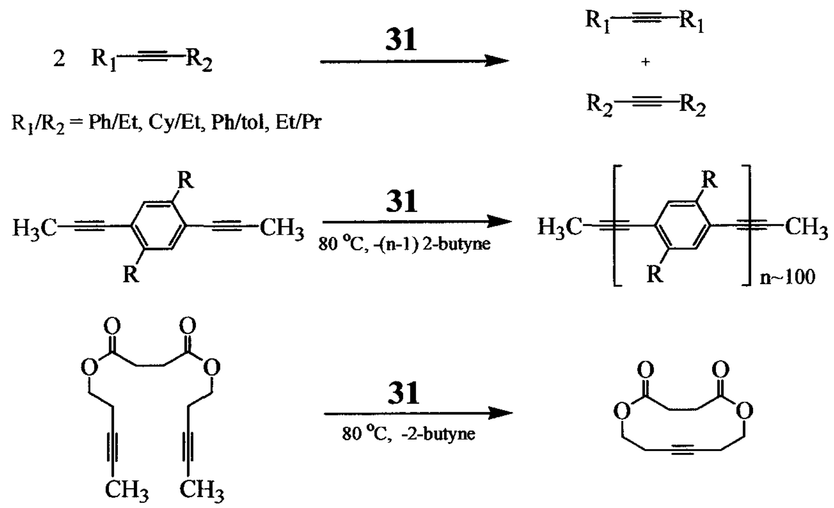
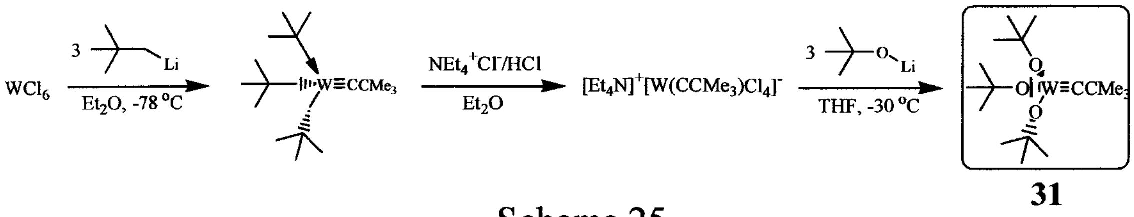
through RCAM with the requirement of shorter reaction times.[53e]

This broad applicability, however, comes at the cost of this complex's difficult preparation and unforgiving handling requirements.



Scheme 24

For instance, the synthesis of **31**, which is outlined in its entirety in Scheme 25, involves the addition of $LiCH_2CMe_3/Et_2O$ to a solution of WCl_6 in Et_2O at -78 °C followed by warming of the reaction mixture to room temperature and sublimation of the air-sensitive $({}^tBuCH_2)_3W{\equiv}C{}^tBu$ from the residue, obtained after solvent removal. This is then treated with $HCl/NEt_4{}^+Cl^-$ in Et_2O, followed by reaction with $LiO{}^tBu$ in THF at -30 °C and subsequent sublimation to give **31** in good yield.



Scheme 25

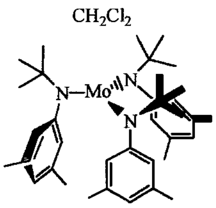
Furthermore, the chemical nature of **31** renders it pyrophoric and precludes its use under any conditions involving even trace amounts of air or moisture. Despite these shortcomings, this system is still regarded as a very effective catalyst for the metathesis of alkyne substrates, and has shown remarkable tolerance toward heteroatom-containing functional groups as outlined in Table 2.[58]

Table 2:

Functional Group Tolerance of $(^t\mathrm{BuO})_3\mathrm{W{\equiv}C}^t\mathrm{Bu}$[47,53ab,e, 58b]
-ester, enolate, ketone, amide
-urethane, ether, alkene
-sulfone, silyl ether, sulfonamide
-acetal, furan

1.4.1.3 *Fürstner's Mo-Based Catalyst: Mo[(N(^{t}Bu)Ar)]$_3$/CH$_2$Cl$_2$*

In an attempt to develop a new catalyst system based on Mo that may be easier to characterize while still very active in a variety of applications, Fürstner *et al.* developed the binary system Mo[N(^{t}Bu)(Ar)]$_3$/CH$_2$Cl$_2$, **32**, which generates an active catalyst species *in situ* upon preparation.[43b] In terms of the identity of the active catalyst, MS and NMR analysis of a solvent-removed residue of **32** identified both [(Ar)(^{t}Bu)N]$_3$MoCl, **33**, and [(Ar)(^{t}Bu)N]$_3$Mo$\equiv$CH, **34**[59] as the primary constituents. This discovery supports the presence of alkylidyne species at the heart of alkyne metathesis reactions, but it is still unknown just how **34** may be formed from **32**.



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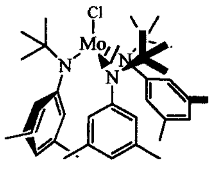

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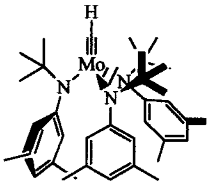
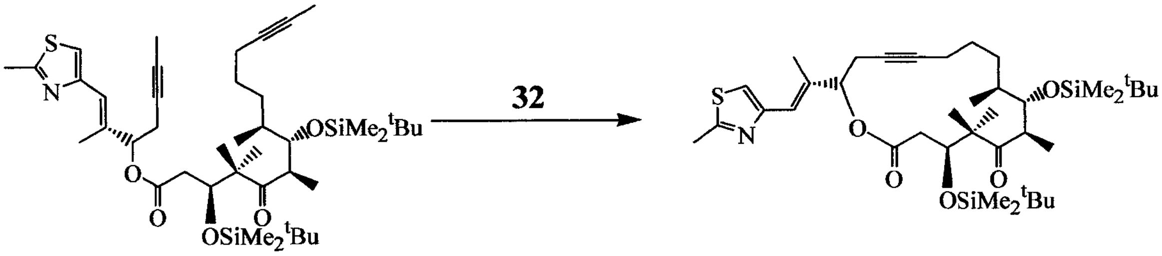


34

The seminal paper describing **32** also detailed its use in both CM and various RCAM processes.[43b] Since then, other CM endeavours undertaken by Fürstner have demonstrated that **32** exhibits a similar activity with alkynes possessing either electron-donating or electron-withdrawing substituents.[60] Another study done by this group showcases the contribution of this system to the synthesis of the macrolide core of the anticancer agents epothilone A/C through RCAM (Scheme 26).[61]



Scheme 26

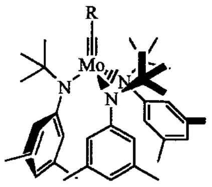
It should also be noted that **32** has been known to tolerate certain functional groups on alkyne substrates that are incompatible with Schrock's catalyst **31** (Table 3; compare with Table 2).[58]

Table 3:

Functional Group Tolerance of Mo[N(^{t}Bu)(Ar)]$_3$/CH$_2$Cl$_2$[60, 43b]
-ketone, alkyl chloride, nitrile, alkene
-ester, tert-amide, ether, silyl ether, acetal, thioether, pyridine
-nitro group, enolate, aldehyde, sulfone, sulfonamide, glycoside

1.4.1.4 *Moore's Mo-Alkylidyne Catalyst: [(Ar)(^{t}Bu)N]$_3$Mo≡CR/phenol*

As a variation of Fürstner's Mo-based system **32**, Moore *et al.* prepared complexes **35**[62] which are analogous to **34**. The synthetic preparation, outlined in Scheme 27 involved the reaction of Mo[N(^{t}Bu)(Ar)]$_3$ with an excess of RCHCl$_2$ (R = H, Me, Et) in THF at ambient temperature to form a mixture of **33** and the desired alkylidynes [(Ar)(^{t}Bu)N]$_3$Mo≡CR, **35**. Mg metal was found to reduce byproduct **33** back to Mo[N(^{t}Bu)(Ar)]$_3$ when added to the reaction mixture resulting in a



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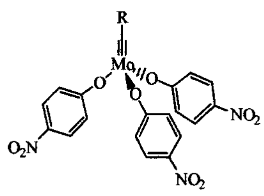
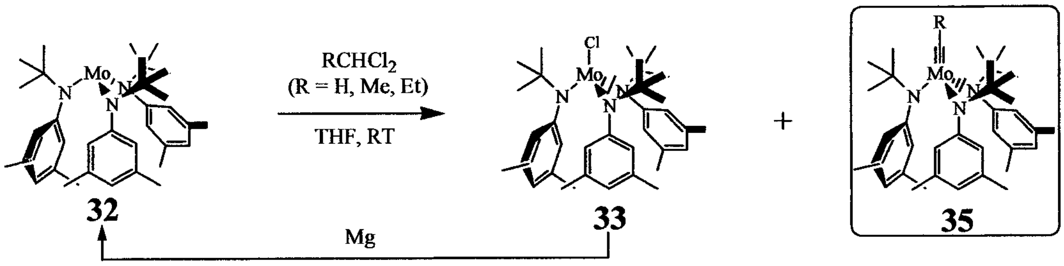


36

recycling of this complex back into the main reaction.[62] In order to be effective in alkyne metathesis, **35** requires the addition of an appropriate substituted phenol to produce the proposed species $(ArO)_3Mo{\equiv}CR$ (ArO = phenoxy ligand), **36**.[63] The most CM-active catalyst in this class resulted from the reaction of **35** (R = Et) with *p*-nitrophenol to produce, presumably, $(p\text{-}NO_2C_6H_4O)_3Mo{\equiv}CEt$.



Scheme 27

It was also found that while monopropynyl substrates carried the advantage of producing 2-butyne upon CM with one another (see Section 1.3 and 1.4.1.1), it is presumed that this byproduct deactivates **36** through rapid polymerization.[64] Therefore, Moore speculates that the higher yields of desired products obtained when using mono*butynyl* substrates are owing to the hindrance of polymerization of the CM byproduct, now 3-hexyne, by this alkyne's increased steric parameters relative to 2-butyne.

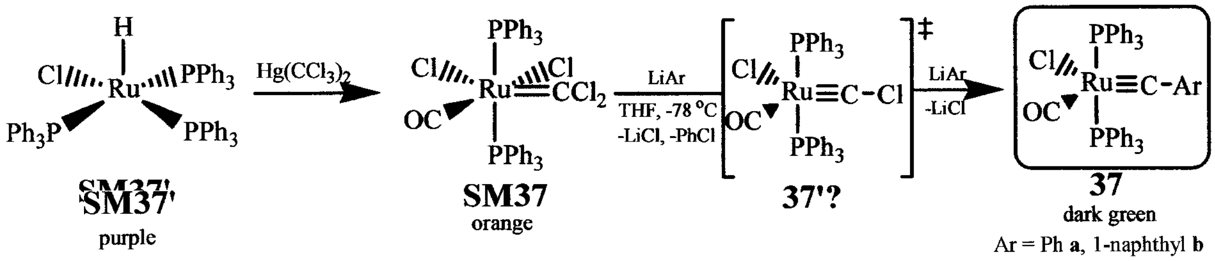
In light of the high alkyne metathesis activity of the above metal-alkylidyne species, it is understandable that their difficult preparation and inherent instability has been overlooked. Since the main cause of this air and moisture sensitivity is likely the high oxophilicity of the early metal centres upon which these complexes are based,[65] it is reasonable to postulate that the use of late transition metal centres in catalyst design may serve to prevent this drawback. Furthermore, the overwhelming success resulting from the use of Ru in olefin metathesis (see Sections 1.1 and 1.2) underscores the high probability of obtaining similar results in the field of alkyne metathesis catalysis.

1.4.2. *Ruthenium-Alkylidyne Complexes*

Until recently, studies aimed toward the stabilization of alkylidyne moeities by Ru coordination centres have been much less prolific than those concerning other areas of Ru chemistry (*e.g.* Ru-based olefin metathesis catalysts, Section 1.2.1.2). This assessment is puzzling given the high logical potential for successful development of revolutionary Ru-based alkyne metathesis systems. In fact, many of the Ru-alkylidynes synthesised to date were obtained completely by accident as unexpected side-products of alkylidene,[71, 90] vinylidene,[79] and allenylidene[84] studies. A couple of unusual Ru-carbide complexes from reactions of Ru-alkylidenes and methylenecyclopropanes,[98] as well as byproducts from olefin metathesis reaction mixtures,[103] have also recently been reported. There have also been studies conducted which have revealed the existence of alkylidyne species on Ru metal surfaces,[105-109] as well as purely homometallic triruthenium clusters containing alkylidyne moieties.[110, 111] While all of these examples of $Ru\equiv C$ bond-containing species are important in their own right, their significance varies in no small extent with their ease of production and stability towards solvents, atmospheric agents, and thermal stresses. In the context of this thesis project, the most synthetically relevant work is that done by Werner (Sections 1.4.2.2 and 1.4.2.4), Valerga (Section 1.4.2.6), and Rigaut and Touchard (Section 1.4.2.7).

1.4.2.1 *Roper's Ru-alkylidynes*

The first well-defined Ru-alkylidyne complexes, the neutral species $Ru(\equiv CPh)Cl(CO)(PPh_3)_2$, **37a**, and $Ru(\equiv C(1\text{-}Naph))Cl(CO)(PPh_3)_2$, **37b**, were prepared by Roper et al. in 1986[66a] and 1998,[66b] respectively. Synthesis of these complexes are based on earlier studies by Roper concerning Os-alkylidyne complexes.[66] Through this method, the dichloro(alkylidene) complex $Ru(=CCl_2)Cl_2(CO)(PPh_3)_2$, **SM37**,[68] is converted to the desired alkyildyne species **37** through treatment with aryllithium reagents, as outlined in Scheme 28.



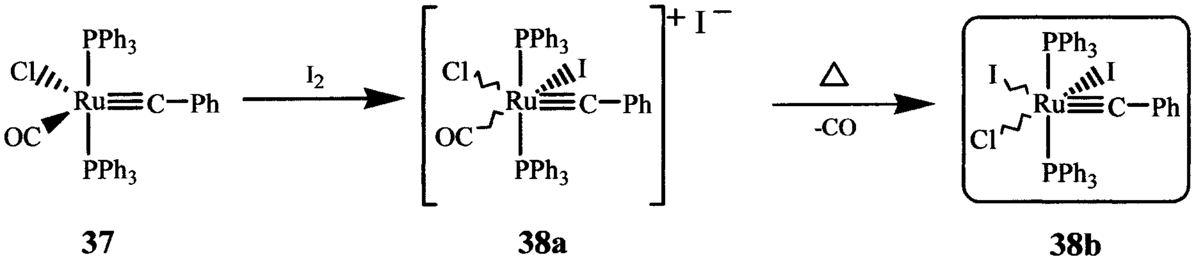
Scheme 28

The key piece of datum that distinguishes **37a** and **37b** as alkylidynes is the presence of strong *v*(CO) absorption bands at 1875 and 1882 cm^{-1}, respectively, in the IR spectra obtained from Nujol mulls of these products. These values are expected for electron-rich carbyne species since the backdonation of electron density into the antibonding orbitals on CO serve to weaken the C-O bond and decrease the frequency of vibration in relation to the value of 2143 cm^{-1} for gaseous CO.[65a] Furthermore, this value for *v*(CO) is similar to that observed for those of Roper's Os-alkylidynes that have been fully structurally characterized.[66b, 67] There are also present medium to weak absorptions at 1328 (**37a**) and 1311 cm^{-1} (**37b**) which have been long-assumed to correspond to molecular vibrations arising from the metal-alkylidyne fragment,[69] another spectroscopic attribute shared by Roper's Os-alkylidynes.

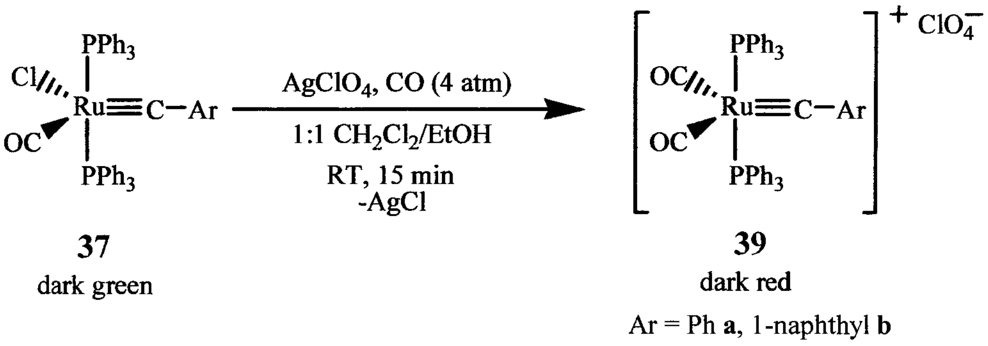
Complexes **37** have also exhibited a tendency towards electrophilic attack by HCl to form the corresponding dichloro(alkylidene) complexes. Furthermore, **37a** will undergo analogous oxidative addition of $HClO_4$ to give a perchloratochloro(alkylidene) species. There is even observed an electrophilic attack at the alkylidyne carbon by $AgClO_4$, in the presence of MeCN, to yield a purple bimetallacyclopropenyl complex. Unfortunately, complexes **37** have also exhibited considerable instability towards water and oxygen, even in the solid phase, decomposing in a few hours upon exposure to the atmosphere.

Elucidation of the most likely mechanism through which this reaction takes place is based mainly on initial studies done on the analogous Os-alkylidyne complex.[67] The first step in the mechanism of this arylation reaction is thought to involve the utility of the first equivalent of LiAr in abstracting both a chloride ligand from the metal, as well as one of the chlorides from the alkylidene moeity, to produce a short-lived chloro(methylidyne) complex **37'**. The abstraction of the chloride from the alkylidyne carbon, accompanied by its concurrent arylation, gives the final product (Scheme 28). This reaction pathway is supported by the observation that the appropriate Os-chloro(benzylidene) did not yield any alkylidyne product upon treatment with LiAr.[67]

During the initial study of Roper's Ru-alkylidyne **37a**, the use of this complex in the preparation of two new alkylidyne complexes through reaction with iodine has also been explored, as illustrated in Scheme 29. The treatment of **37a** with elemental iodine affords the cationic chloroiodo-(alkylidyne), **38a**, which loses CO upon heating to give the neutral chloroiodo(alkylidyne), **38b**. In addition to this work, Roper devised a method of producing cationic Ru-alkylidynes $[Ru(\equiv CPh)(CO)_2(PPh_3)_2]ClO_4$, **39a**, and $[Ru(\equiv C(1\text{-}naphthyl))(CO)_2(PPh_3)_2]ClO_4$, **39b**, by reacting complexes **37** with $AgClO_4$ and CO (Scheme 30).[66]



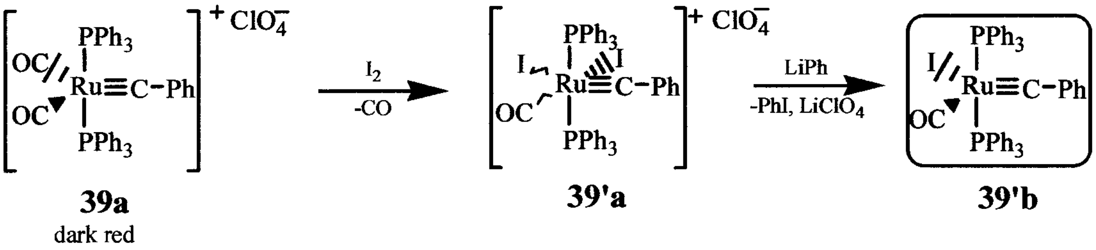
Scheme 29



Scheme 30

The IR analysis of complexes **39** reveal two strong *v*(CO) absorption bands for each complex; 2020 and 1960 cm^{-1} for **39a**, and 2009 and 1920 cm^{-1} for **39b**. These higher vibration frequencies likely indicate the expected decrease in the amount of backdonation of electron density to CO by the cationic Ru-alkylidyne fragments relative to their neutral analogues. The characteristic medium absorption bands corresponding to the metal-alkylidyne fragments are also present at 1370 cm^{-1} for **39a** and 1317 cm^{-1} for **39b**.

In contrast to **37**, complexes **39** are much more stable toward air, moisture and electrophilic attack, an attribute which is foreshadowed by the cationic nature of these species. However, as Scheme 31 indicates, **39a** has been known to undergo oxidative addition of elemental iodine with concomitant loss of CO to form the cationic diiodo(alkylidyne) complex **39'a**. This complex will then react with PhLi to generate the neutral five-coordinate alkylidyne species **39'b**.



Scheme 31

For synthetic chemists, there is much room for improvement in terms of preparation of the alkylidyne complexes. Unfortunately, synthetic methods that are likely to be used on a broad scale in the future are not likely to include such undesirable reagents as toxic mercurials and potentially explosive perchlorate salts in their methodology. Clearly safer and more convenient methods of alkylidyne production are required.

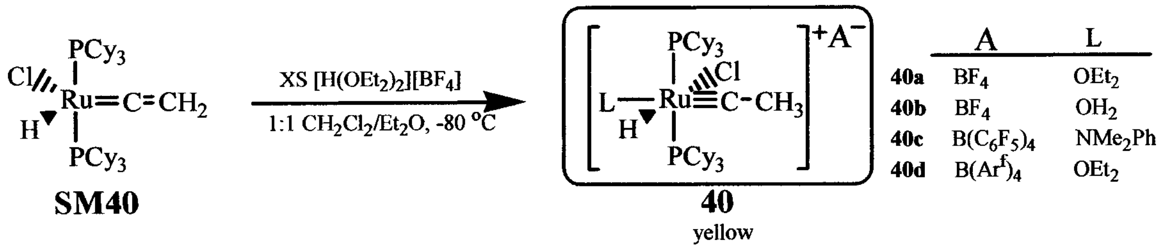
1.4.2.2 *Werner's Monocationic Ruthenium Alkylidynes*

1.4.2.2.1 *Six-coordinate Ruthenium Hydrido(alkylidynes), $[RuHCl(S)(\equiv CCH_3)(PCy_3)_2]A$*

While attempting to prepare a new class of coordinatively unsaturated cationic Ru-alkylidene complexes,[70] Werner et al. in 1998[71] reported the first discovery of a new class of well-defined Ru-alkylidyne species since those described by Roper et al. in 1986 (Section 1.4.2.1). At the time, it was thought that treatment of hydrido(vinylidene) species with HA (A = noncoordinating anion) may readily yield these species. Instead, the resultant solvent-stabilized hydrido(alkylidyne) species $[RuHCl(S)(\equiv CCH_3)(PCy_3)_2]A$, **40** (S = solvent, A = counteranion), were obtained as the sole products. This revelation was supported by NMR spectroscopy with the absence of the low-field signal corresponding to a hydrogen atom which is bonded to C_α of an alkylidene moeity. Also, the persistence of the high-field signal ($\sim \delta -6$ ppm) associated with a metal-bound hydride ligand reinforced the proposed product identity. This experimental method had precedent since there had been other examples of alkylidynes formed upon protonation of vinylidenes.[72]

The preparation methods for each member of this class closely resemble one another, as Scheme 32 indicates. For the first prepared example of this group, protonation of the appropriate hydrido(vinylidene) precursor $RuHCl(=C=CH_2)(PCy_3)_2$, **SM40**[73] was carried out using HBF_4/Et_2O in a 1:1 CH_2Cl_2/Et_2O medium at -80 °C. Gradual warming of the reaction mixture to ambient temperatures was followed by solvent removal *in vacuo* and crystallization of the yellow product **40a** with Et_2O addition. Complex **40b** was obtained simply by shaking a sample of **40a** in CH_2Cl_2 with degassed H_2O for 1 minute, then separating the organic phase to give yellow **40b** upon solvent removal. Conversely, **40c** and **40d** were formed in an NMR tube in CD_2Cl_2 through treatment of **SM40** with the appropriate protic agents, these being $[HNMe_2Ph][B(C_6F_5)_4]$ for **40c** and $[H(Et_2O)_2][B(Ar^f)_4]$[74] for **40d**.

Since there are two potential pathways for this protonation reaction to occur, one



Scheme 32

involving initial attack of the proton directly at C_β and another at the metal[75] followed by migration to C_β, the authors carried out a deuterium labelling experiment using $[DNMe_2Ph][B(C_6F_5)_4]$ as the deuterating agent under NMR conditions. The authors postulated that if there was a competing attack taking place at the metal, there would be at least some of the deuteroalkylidyne complex $[RuDCl(S)(\equiv CCH_3)(PCy_3)_2][B(C_6F_5)_4]$ observed after reaction completion. The absence of this species from the acquired D NMR spectra was taken as an indication that there is very little deuteron attack occurring at the metal, if at all.

The ^1H NMR spectra of complexes **40** all include the characteristic metal hydride signals in the area of δ −6 ppm. There are also present in the ^{13}C NMR spectra of **40a-c** low-field signals around δ 310 ppm corresponding to the alkylidyne carbon atoms (Table 4). Interestingly, only the signal obtained from NMR analysis of **40a** shows resolved splitting due to the coupling of the alkylidyne signal with that of the P-atoms of the PCy_3 ligands, while **40b** and **40c** exhibited broad singlets. ^{13}C NMR analysis was not carried out for **40d**.

Surprisingly, the activity of **40a** in the ROMP of cyclic olefins constitutes the first example of a metathesis-active Ru-alkylidyne. In fact, a comparison study exhibited the ROMP of cyclooctene by **40a** occurring about 20 times faster than by Grubbs' catalyst **5**. **40a** has also effected the CM of cyclopentene, using the electron-poor olefin methyl acrylate as the chain transfer agent, thereby yielding long-chain functionalized olefins as the key products. Some initial studies conducted by the authors seem to indicate that complexes **40b-d** possess similar metathesis activity, albeit not as pronounced as that of **40a**.

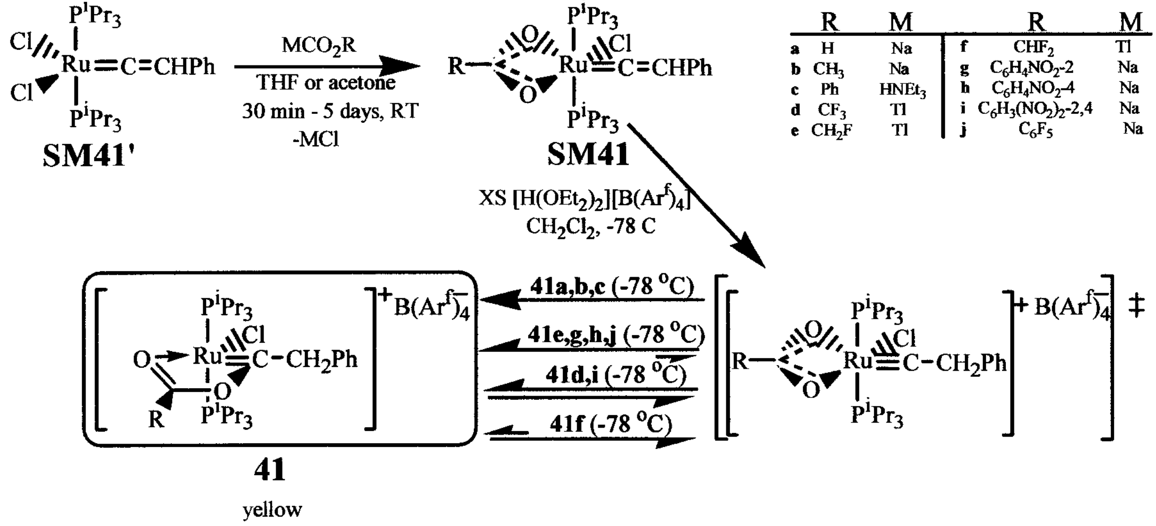
The observed stabilities of complexes **40** have left much to be desired, with each complex completely decomposing in solution within a few hours at room temperature. This decomposition is thought to involve deprotonation and dissociative loss of coordinated solvent since the addition of excess amounts of the appropriate solvent or acid to solutions of **40** extends their stability for hours. Furthermore, complexes **40c** and **40d** have only been observed in solution, and **40c** is unstable above -60 °C.

1.4.2.2.2 *Six-coordinate Ruthenium η^2-Carboxylato(alkylidynes),* *$[RuCl(\eta^2\text{-}O_2CR)(\equiv CCH_2Ph)(P^iPr_3)_2]B(Ar^f)_4$*

With the extreme instability of the previously-reported complexes **40** presenting a crippling obstacle to widespread application of these species, Werner et al. aimed to amend these shortcomings through preparation of more stable Ru-alkylidynes. So, in 2000,[76] they attempted the incorporation of chelating carboxylate ligands into the design of their Ru-alkylidynes.

The authors' synthetic approach, outlined in Scheme 33, entailed first the conversion of the parent dichloro(vinylidene) $RuCl_2(=C=CHPh)(P^iPr_3)_2$, **SM41'**,[77] into the corresponding carboxylato(vinylidene) complexes **SM41**. The protonation of these species was carried out at -78 °C in CH_2Cl_2 using freshly prepared $[H(Et_2O)_2][B(Ar^f)_4]$ followed by warming to ambient temperatures and precipitation of yellow products $[RuCl(\eta^2\text{-}O_2CR)\text{-}(\equiv CCH_2Ph)(P^iPr_3)_2]B(Ar^f)_4$, **41**, by addition of pentane.

At this point, it was assumed that the expected products had probably been formed since the NMR data agreed with what they had anticipated. Unfortunately, the single-crystal X-ray structure obtained for R = H, **41a**, revealed that the product was in fact the Ru-alkylidene which results from the nucleophilic attack of the alkylidyne C-atom by one of the carboxylate O-atoms. The authors postulate the involvement of an alkylidyne species as the first intermediate in the mechanism of this rearrangement which then undergoes a 1,2-shift of one of the weakly bound carboxylate O-atoms to the alkylidyne carbon to form the more stable alkylidene species. The same conclusions were drawn for the products in which R = Me (**41b**) and R = Ph (**41c**).[76]



	R	M		R	M
a	H	Na	f	CHF_2	Tl
b	CH_3	Na	g	$C_6H_4NO_2$-2	Na
c	Ph	$HNEt_3$	h	$C_6H_4NO_2$-4	Na
d	CF_3	Tl	i	$C_6H_3(NO_2)_2$-2,4	Na
e	CH_2F	Tl	j	C_6F_5	Na

Scheme 33

A completely different and altogether surprising result was obtained for the product with R = CF_3 (**41d**). It seems this electron-deficient carboxylate ligand is less able to attack the electrophilic alkylidyne carbon atom due to the strongly electron-withdrawing nature of the F-atoms of the CF_3 group. There is in fact an equilibrium observed between the six-coordinate alkylidyne and five-coordinate alkylidene species that seems to depend strongly on the temperature of the reaction medium. A variable-temperature ^{31}P NMR experiment revealed the presence of two distinct species at low temperatures (−83 °C), each represented by a sharp singlet at δ 61 and 50.8 ppm, respectively. As the temperature was increased, these signals broaden (~ −40 °C) and finally coalesce into a single peak (δ 56.5 ppm) at room temperature (23 °C).

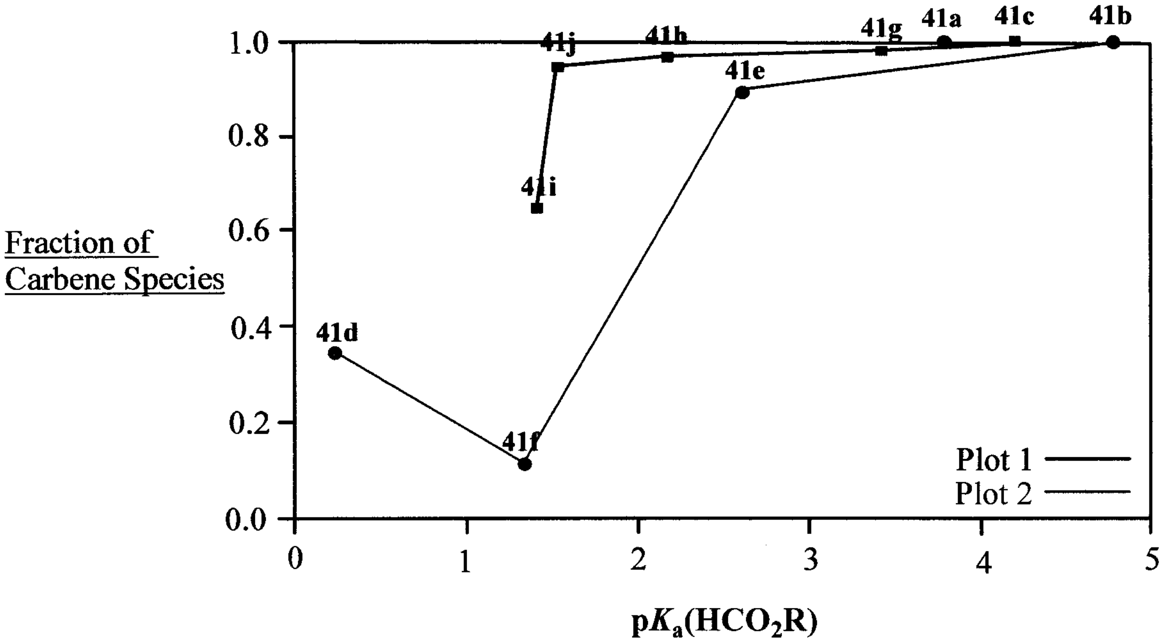
Similar spectroscopic features were observed upon ^1H NMR analysis with two low-temperature (-83 °C) signals at δ 5.20 and 4.59 ppm (integral ratio 1:2) which are assigned to the CH_2Ph protons of each species. These signals also broaden (~ −45 °C) and coalesce into one signal at δ 4.88 ppm at ambient temperature. This data is indicative of the majority presence of an alkylidyne species at low temperatures since the larger signal at δ 4.59 ppm is very similar to the analogous signal of

$[RuCl_2(\equiv CCH_2Ph)(P^iPr_3)_2][B(Ar^f)_4]$.[78] Similarly, the lesser signal at δ 5.20 ppm is very close to the analogous signals of the structurally characterized alkylidene complexes **41a-c**, thereby implying that this signal corresponds to an alkylidene species. Furthermore, an X-ray crystal structure solved for single crystals grown from a solution of **41d** in CH_2Cl_2 at −78 °C confirmed that the majority isomer at this temperature was in fact an alkylidyne species (~66% based on integrals of CH_2Ph ^{1}H NMR signals). An interesting attribute of this complex is the Ru≡C bond length of 1.660 Å, which was one of the shortest M≡C bond lengths known at the time of publication.[51]

Further studies on this class of complexes were published by this group in 2001[78] and included the utility of several more electron-deficient carboxylate ligands in attempted syntheses, also outlined in Scheme 33, which were analogous to those reported in 2000. The resultant complexes **41e-j** all exhibited structural equilibria similar to that of **41d**, albeit to different extents. For instance, in the case of complexes **41e**, **g**, **h**, and **j** this equilibrium almost exclusively favours the alkylidene species at −78 °C, whereas **41i** shows the presence of ~35% of the alkylidyne isomer. Surprisingly, complex **41f**, which includes $-CHF_2$ as it's carboxylato functional group, was observed to strongly favour the alkylidyne isomer (88%) despite the fact that it is comparatively less electron-withdrawing relative to $-CF_3$.

It is also argued by the authors that the relative amounts of the alkylidene and alkylidyne isomers may be shown to depend on the basicity of the carboxylate ligand (Figure 5), which may be measured to some extent using the pKa values of the corresponding carboxylic acids in aqueous solution. For the benzato complexes **41c** and **g-j**, this correlation works nicely with the relative proportion of the alkylidene isomer increasing as does the basicity of the carboxylate ligand, as measured by the pKa of the corresponding acid (Figure 5, plot 1). However, the acetato complexes **41b** and **d-f** deviate from this proposed trend in that **41f** favours the alkylidyne isomer much more than **41d**, which possesses the more basic carboxylato ligand (Figure 5, plot 2).

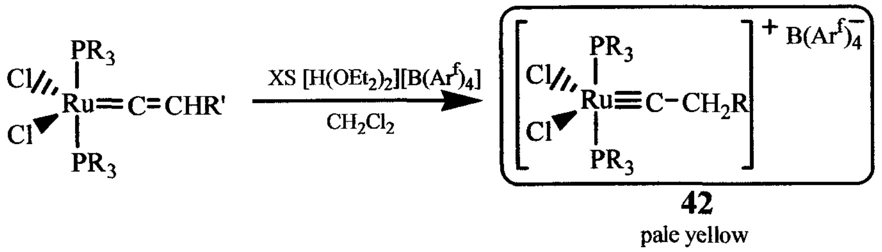
Figure 5: Plot of $\chi_{carbene}$ *vs.* pKa(HCO_2R) for Complexes 41



1.4.2.2.3 *Five-Coordinate Ruthenium Dichloro(alkylidynes),*
$[RuCl_2(\equiv CCH_2R)(PR_3)_2]B(Ar^f)_4$

During the course of their research concerning the study of the structural equilibria of complexes **41** (Section 1.4.2.2.2), Werner et al.[78] attempted the preparation of new Ru-alkylidynes through protonation of the dichloro(vinylidene) precursor complex $RuCl_2(=C=CHPh)(P^iPr_3)_2$, **SM41'**, as well as three other similar complexes **SM42a-c**.

As with **SM40** and **SM41** before, protonation of the parent vinylidenes was carried out using $[H(Et_2O)_2][B(Ar^f)_4]$ in CH_2Cl_2 at room temperature for **SM41'** and **SM42a,b**, and at -20 °C for **SM42c**. The desired pale yellow alkylidyne complexes $[RuCl_2(\equiv CCH_2R)(PR_3)_2][B(Ar^f)_4]$, **42**, were obtained nearly quantitatively through concentration of the reaction mixture *in vacuo* followed by precipitation with pentane addition. These preparations are illustrated in Scheme 34. The characterization of



	PR_3	R'
42a	P^iPr_3	Ph
42b	P^iPr_3	^tBu
42c	PCy_3	Ph
42d	PCy_3	^tBu

Scheme 34

complexes **42** was effected in much the same way as in previous studies. The X-ray crystal structure obtained for **42b** confirmed the identity of this complex as an alkylidyne species possessing an unusually short Ru≡C bond length of 1.660 Å.[51] With this confirmed structure in hand, the acquisition of analogous NMR data for **42a**, **c** and **d** provide sufficient evidence for the characterization of these species as alkylidynes. Important features of these analyses include of course the low-field triplet signals in the ^{13}C NMR spectra around δ 310 ppm for **42a** and **b** and δ 317 ppm for **42c** and **d** which are assignable to the alkylidyne carbons coupled with the P-atoms of the phosphine ligands ($^2J_{PC}$ = ~4-5 Hz) (Table 4). There are also observed analogous triplet signals in the ^1H NMR spectra at δ ~4.50 ppm for **42a** and **b** and δ ~3.30 ppm for **42c** and **d** which correspond to the CH_2R protons. Also, the attempted use of low-temperature NMR practices toward the detection of some metal-bound hydride resulting from the possible initial protonation of the metal atom failed to reveal the presence of this species as an intermediate in the protonation reaction due to the near-instantaneous formation of the alkyidyne complex.

The stability of complexes **42** are on the whole higher than that observed for complexes **40** (Section 1.4.2.2.1). While only moderately air-stable in the solid state, solutions of **42a** and **b** in exhaustively dried $CHCl_3$ can stand for days at room temperature before complete decomposition. **42c** and **d**, on the other hand, are unable to last 24 hours in dry $CHCl_3$ without complete decomposition, yielding $[HPR_3][B(Ar^f)_4]$ in the process. This implies that the decomposition pathway involves the dissociation of a phosphine ligand, followed by deprotonation of alkylidyne molecules by these ligands to

Table 4: Summary of Spectroscopic Data for Complexes in Section 1.4.2

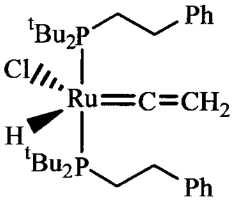
Complex	Ru≡C Bond Length (Å)	^{13}C NMR δ-values of C_α (ppm)	Muliplicity ($^2J_{PC}$(Hz))
40a	N/A	316.1	t,(9)
40b	N/A	314.0	br s
40c	N/A	311.9	br s
41d	1.660	N/A	N/A
41f	N/A	330.0 (243 K)	t, (7.6)
42a	1.660	310.0	t, (5.1)
42b	N/A	317.7	t, (3.8)
42c	N/A	309.7	t, (4.4)
42d	N/A	317.0	t, (3.8)
44a (R = Cy)	N/A	260.5	t, (21)
44b (R = ^{i}Pr)	1.873	247.9	t. (20)
45	2.000	250.2	N/A
46	N/A	315	dd, both (14.6)
47	1.696	304.5	t, (13.7)
48a	N/A	332.4	t, (13.1)
48b	1.766	327.5	t, (12.5)
49a	N/A	307.74	quint, (13)
49b	N/A	323.05	N/A
50	N/A	314.13	N/A
51	1.632	471.5	s
52	1.650	479.64	s
54	1.662	381.23	m
55	N/A	446.31	s
56	1.698	414.0	d, $^2J_{HC}$ = (10.4)

give as yet unidentified ruthenium complexes and the aforementioned phosphonium salts.

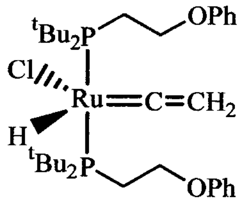
Interestingly, complexes **42a** and **b** exhibit ROMP activity similar to that of **40**, although not as pronounced. The addition of 1 mol% of these complexes to cyclooctene in CH_2Cl_2 causes the thickening of the reaction mixture after 6 hours and complete monomer consumption after 20 hours. During reaction, the alkylidyne complexes remain the sole ruthenium-based species detectable by NMR spectroscopy, the amounts of which do not greatly decrease after 6 hours. The aforementioned phosphonium species $[HPR_3][B(Ar^f)_4]$ is also present in the reaction mixture, an observation that the authors view as an indication that the active catalytic species is actually formed upon dissociation of a phosphine ligand followed by deprotonation of the alkylidyne moeity to form an olefin metathesis-active vinylidene complex. This would not be the first instance of olefin metathesis effected by Ru-vinylidene complexes (Section 1.2.2.3).

1.4.2.2.4 *Werner's in situ Ruthenium-Alkylidyne*

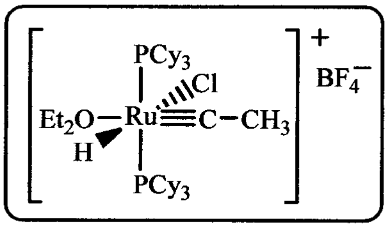
During an investigation of the binding behaviour of the potentially tetradentate phosphine ligands $^tBu_2P(CH_2)_2Ph$ and $^tBu_2P(CH_2)_2OPh$ in Ru-vinylidene and -allenylidene complexes,[79] Werner et al. noticed that their prepared vinylidene complexes $RuHCl(=C=CH_2)(^tBu_2P(CH_2)_2Ph)_2$, **SM43a**, and $RuHCl(=C=CH_2)(^tBu_2P(CH_2)_2OPh)_2$, **SM43b**, would efficiently catalyze the ROMP of cyclooctene under NMR conditions in CD_2Cl_2 with the addition of HBF_4/Et_2O reagent.



SM43a



SM43b



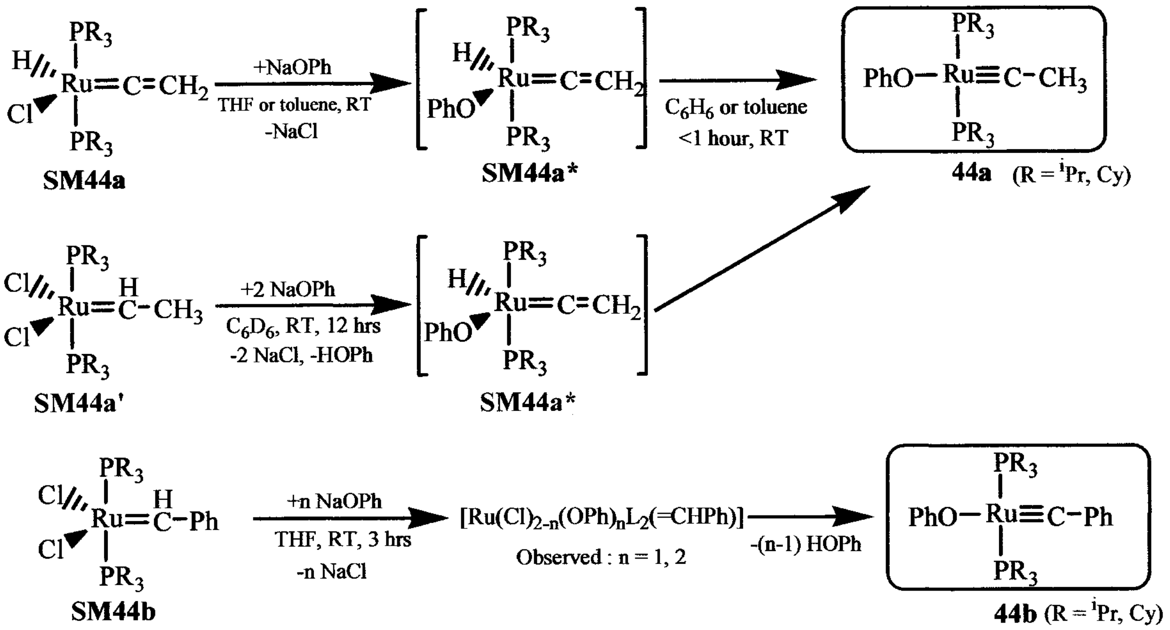
43a

The active catalyst species, which were observed to be more active in this capacity than Grubbs'-catalyst **5**, were postulated as being alkylidyne species which are structurally analogous to complexes **40** (Section 1.4.2.2.1), as indicated by NMR analysis of $[RuHCl(\equiv C-CH_3)-(^tBu_2P(CH_2)_2Ph)_2]BF_4$, **43a**. The main distinguishing features of these spectra include the increase in the relative integral of the triplet signal at $\delta \sim 2.63$ ppm from 2 H (for $=CH_2$ of vinylidene) to 3 H (for $-CH_3$ of alkylidyne), as well as the change in position of the high-field hydride signal from $\delta -15.80$ to -7.63 ppm. This latter feature is understandable since the assumption of an overall cationic charge by the complex would likely result in a decreased shielding of the hydride ligand thereby shifting it's respective signal to a lower-field value. Also, in contrast to **SM43a**, the hydride ligand of **43a** is *trans* to a chloride ligand which likely causes the observed decreased shielding of this proton.[79]

1.4.2.3 *Caulton and Eisenstein's Neutral Four-Coordinate Ruthenium Alkylidynes, $Ru(OPh)(\equiv CR')(PR_3)_2$*

Prompted by the utility of five-coordinate metal-vinylidene complexes as catalytic precursors to a variety of organometallic reactions,[80] Caulton et al. in 2000[81] attempted the preparation of the four-coordinate alkylidyne complexes which are structural isomers to these vinylidenes. They in fact succeeded in producing four such complexes: $Ru(OPh)(\equiv CCH_3)(PR_3)_2$, **44a**, and $Ru(OPh)(\equiv CPh)(PR_3)_2$, **44b** ($R = {}^iPr$, Cy), using the appropriate parent hydrido(vinylidene) compounds $RuHCl(PR_3)_2(=C=CH_2)$, **SM44a**,[12c, 77b] as well as Grubbs' alkylidene complexes $RuCl_2(=CHCH_3)(PR_3)_2$, **SM44a'**, and $RuCl_2(=CHPh)(PR_3)_2$, **SM44b**[11b] ($R = {}^iPr$, Cy). These preparations are outlined in Scheme 35.

The preparation of **44a** was effected by treatment of **SM44a'** with NaOPh with the elimination of NaCl and the formation of the phenoxy(vinylidene) complexes $RuH(OPh)(PR_3)_2(=C=CH_2)$, **SM44a***. These molecules are observed to rearrange in arene solvents, such as benzene or toluene, to give the four-coordinate alkylidyne isomers, a process which occurs spontaneously over a period of an hour or so. Curiously, the analogous Ph-substituted phenoxy(vinylidene) $RuH(OPh)(PR_3)_2(=C=CHPh)$ does not



Scheme 35

undergo this same rearrangement for reasons of conjugative stabilization of the vinylidene species by the aromatic ring of the Ph group, as postulated by the authors.

The successful formation of **44a** was established on the basis of ^{1}H and ^{13}C NMR analysis. The $-CH_3$ protons appear in the ^{1}H NMR spectra between 0 and -0.5 ppm which is characteristic of ethylidyne complexes involving late transition metals.[82] Most indicative is the disappearance of the ^{13}C signals around δ 88 ppm, which correspond to C_β of the vinylidene, and the appearance of ^{13}C signals around δ 28 ppm for the CH_3 carbons of the ethylidyne ligand. The disappearance of the high-field ^{1}H signal around δ -16 ppm for the hydride ligand is also supportive of the proposed product structure.

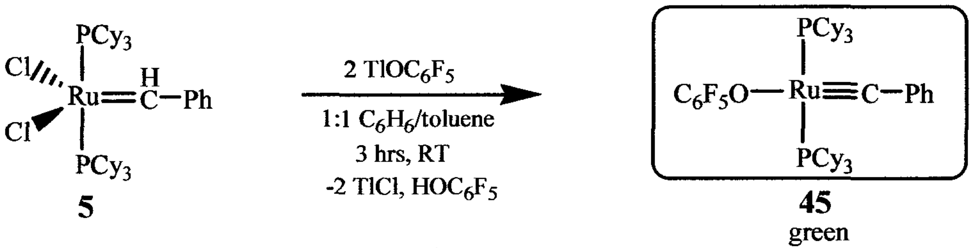
The use of the Grubbs-type dichloro(alkylidene) complexes $RuCl_2(=CHCH_3)(PR_3)_2$, **SM44a'**, as precursors to the formation of the corresponding vinylidene complexes was also found to yield phenoxy(alkylidyne) species. Upon reaction of **SM44a'** with two equiv. of NaOPh in C_6D_6, 12 hours of reaction yielded the desired phenoxy(alkylidynes) **44a** accompanied by NaCl precipitation and elimination of phenol as indicated by NMR spectroscopy.

In order to obtain the dichloro(benzylidyne) complexes $Ru(OPh)(\equiv CPh)(PR_3)_2$,

44b, the Grubbs-type benzylidene complexes **SM44b** were reacted with two equiv. of NaOPh in THF to yield the corresponding bis(phenoxy)(alkylidenes) with concomitant loss of NaCl and phenol. Further phenol elimination results in the formation of the desired products **44b** within 3 hours of reaction.

The characterization of **44b** (R = ^{i}Pr) by X-ray crystallography irrevocably confirms the alkylidyne structure of this complex. One feature of note is the Ru≡C bond length of 1.873 Å, which is significantly longer than that of complexes **41d** (Section 1.4.2.2.2) and **42b** (Section 1.4.2.2.3). This structure, coupled with NMR data, provides a sense of associative characterization of complexes **44a** since the NMR data are largely similar. To date, these compounds have shown no activity in metathesis reactions.

Another member of this class of four-coordinate alkylidynes, $Ru(OC_6F_5)(\equiv CPh)(PCy_3)_2$, **45**, is one that was prepared by Fogg et al. in 2003[83] using Grubbs'-catalyst **5** as a precursor (Scheme 36).



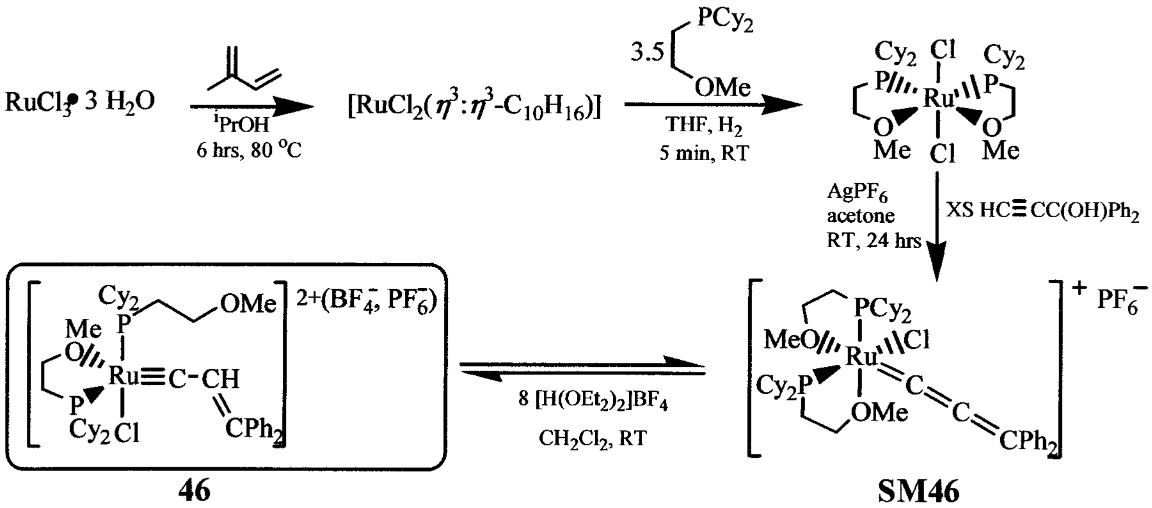
Scheme 36

In addition to the obvious ^1H NMR spectral features (*e.g.* disappearance of low-field alkylidene proton and high-field hydride ligand signals), **45** has been characterized by X-ray crystallography using single crystals obtained through deposition from benzene solutions. One interesting feature obtained from this structure is the inordinately long Ru≡C bond length of 2.00 Å, which is the longest Ru–C bond length mentioned in this thesis so far and is certainly among the longest M≡C bond lengths reported thus far.[51]

1.4.2.4 *Werner's Dicationic Ruthenium Vinyl(alkylidyne),* $[RuCl(\equiv C\text{-}CH{=}CPh_2)(\eta^2\text{-}P,O\text{-}Cy_2P(CH_2)_2OMe)(\eta^1\text{-}P\text{-}Cy_2P(CH_2)_2OMe)][BF_4, PF_6]_2$

In the quest for more effective olefin metathesis catalyst species, Werner et al. in 2001[84] employed the chelating bidentate phosphinoether ligands $Cy_2P(CH_2)_2OMe$ in the straightforward production of the allenylidene complex $[RuCl(=C=C=CPh_2)(\eta^2\text{-}P,O\text{-}Cy_2P(CH_2)_2OMe)(\eta^2\text{-}P\text{-}Cy_2P(CH_2)_2OMe)]PF_6$, **SM46**.[85] Once this complex exhibited less activity in the ROMP of cyclooctene and RCM of *N,N*-diallytosyl amide, when compared to another allenylidene complex $[(p\text{-cymene})RuCl(=C=C=CPh_2)(PCy_3)]^+$ introduced by Dixneuf and Fürstner in 1998,[86] they discovered that the popular acid $[H(Et_2O)_2][BF_4]$ is capable of protonating C_β of **SM46** in much the same way as with vinylidene complexes (Section 1.4.2.2). The protonation of allenylidene species by HBF_4 has been previously reported,[87] and a nucleophilic character at C_β of some Ru-allenylidene complexes has also been predicted through theoretical calculations.[88]

The experimental method used by the authors for producing the precursor to the allenylidene **SM46** involves a procedure which is slightly modified from the traditional method (Scheme 37).[89] Complex **SM46** was then dissolved in CH_2Cl_2 and treated with



Scheme 37

eight equiv. of HBF_4 in the form of $[H(Et_2O)_2][BF_4]$. The stirring of the reaction mixture at room temperature resulted in an almost instantaneous colour change from red to green. NMR analysis of the residue confirmed the successful production of the desired complex $[RuCl(\equiv C-CH{=}CPh_2)(\eta^2\text{-}P,O\text{-}Cy_2P(CH_2)_2OMe)(\eta^1\text{-}P\text{-}Cy_2P(CH_2)_2OMe)][BF_4, PF_6]_2$, **46**, but all attempts at recrystallization from CH_2Cl_2/Et_2O mixtures resulted in the regeneration of **SM46** due to the highly reversible nature of this protonation.

Key features of **46** were derived from both the ^1H and ^{13}C NMR spectra obtained from these experiments. For instance, in the ^{13}C NMR spectrum, the disappearance of the signal for C_α of **SM46** at δ 301.2 ppm is accompanied by the appearance of the alkylidyne carbon signal at δ 315 ppm. Similarly, the signals corresponding to C_β and $C\gamma$ are moved from δ 220 and 152.4 ppm to δ 129.7 and 184.6 ppm, respectively. In the ^1H NMR spectrum, the appearance of the vinylic proton signal at δ 6.37 ppm is perhaps most indicative of the successful protonation of C_β. In addition, the two singlets which correspond to the protons of the coordinated OMe groups move from the close values of δ 3.99 and 3.9 ppm to δ 4.06 and 3.39 ppm, thereby strongly supporting the fact that this protonation has resulted in the dissociation of one of the –OMe groups.

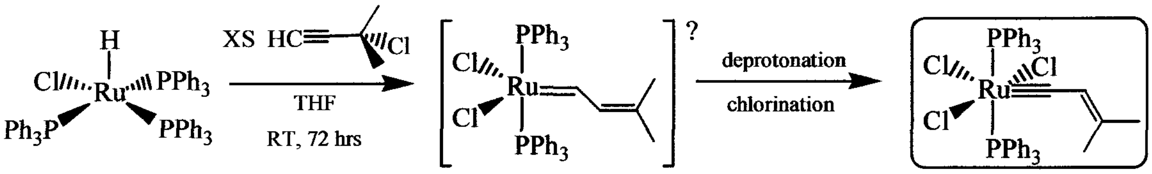
A brief investigation of the catalytic activity of **46** has revealed that this complex is less active in olefin metathesis compared to alkylidynes with the molecular unit $RuHCl(\equiv CCH_3)$, but details of these studies were not published.[84]

1.4.2.5 *Fogg's Neutral Ruthenium Trichlorovinyl(alkylidyne), $RuCl_3(PPh_3)_2(\equiv CCH{=}CMe_2)$*

During the development of a much safer and easier method of producing Grubbs-type alkylidene complexes from easily produced or commercially available starting materials, Fogg et al. in 2002[90] discovered a new Ru-alkylidyne complex which was formed as a byproduct during their core reaction.

The use of the commercially available $RuHCl(PPh_3)_3$, **SM47**, by the authors constitutes perhaps the safest one-step method for producing Ru-alkylidenes reported so far. Through this method, **SM47** is treated with a slight excess of 3-chloro-3-methyl-1-butyne in CH_2Cl_2. The authors noticed that if PCy_3 is added to the reaction mixture at this point, the Ru-alkylidyne complex $RuCl_3(PPh_3)_2(\equiv CCH{=}CMe_2)$, **47**, is isolated.

While the amount of **47** produced is small when performing this reaction in CH_2Cl_2, it was found that using a fourfold excess 3-chloro-3-methyl-1-butyne and changing the solvent to THF resulted in an approximate isolated yield of 75% for **47** (Scheme 38). The reaction mechanism is thought to involve the formation of the intermediate vinyl(alkylidene) species $RuCl_2(PPh_3)_2(=CCH{=}CMe_2)$, **SM47***, originally the desired product of the cited paper, which somehow undergoes deprotonation and chlorination to yield **47**.[90]



SM47 **SM47*** **47**

orange

Scheme 38

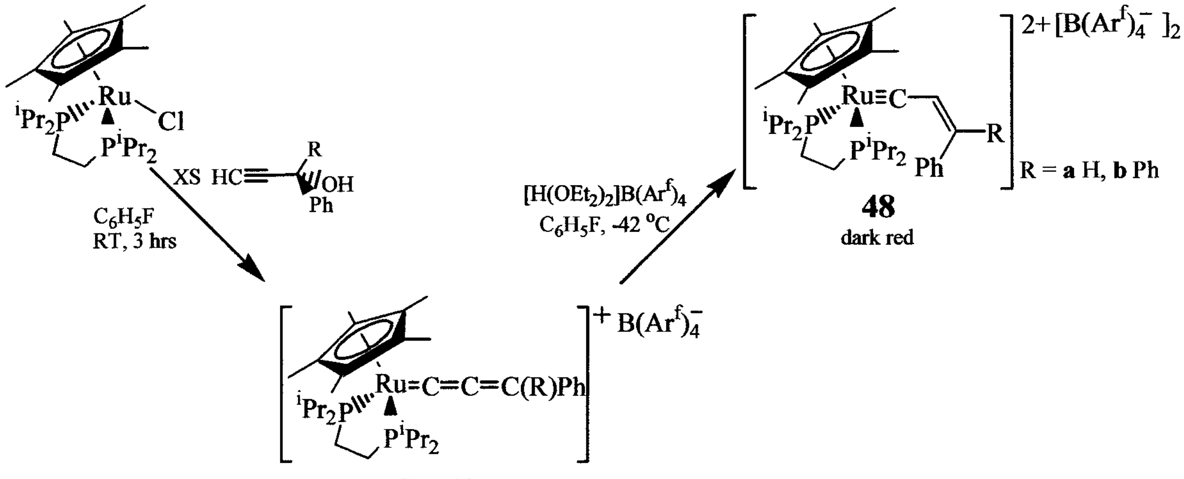
The characterization of **47** by X-ray crystallography was also accompanied by supportive ^1H and ^{13}C NMR analyses. In addition to the characteristic low-field ^{13}C signal at δ 304.5 ppm for the alkylidyne carbon, ^1H-^{13}C HMQC experiments, which measure the high H-C coupling constants of proton-bonded carbons, were also carried out. Through these experiments, it was shown that the olefinic proton signal at δ 4.39 ppm corresponds with the singlet in the ^{13}C NMR spectrum at δ 130.5 ppm, which was otherwise overshadowed by the Ph-signals of PPh_3. ^1H-^{13}C HMBC experiments, which measure weak H-C coupling constants (*i.e.* H may be up to four bonds from C in question), were employed to confirm that the ^{13}C signal at δ 183.5 ppm in fact corresponds to the quaternary $=CPh_2$ carbon. This signal is postulated by the authors to be so far down field due to some vinylidene resonance contributor in which this carbon has a formal negative charge (*i.e.* highly deshielded). From the X-ray crystal structure, the somewhat shorter than average Ru≡C bond length of 1.696 Å is perhaps the most notable feature.[90]

There were no investigations of the catalytic activity of **47** towards the metathesis of olefin substrates in the cited paper, nor were there any comments on the stability of this material. Therefore, the main significance of this study is that it proves that the production of Ru-alkylidenes and -alkylidynes doesn't necessarily have to include the use of hazardous reagents such as diphenylcyclopropene[9,10] and diazoalkanes.[11]

1.4.2.6 *Valerga's Dicationic Ruthenium Diphosphinovinyl(alkylidynes),* $[Cp^*Ru(\equiv CCH{=}C(R)Ph)(dippe)][B(Ar^f)_4]_2$

In 2002,[91] Valerga et al. reported the preparation of new dicationic vinyl(alkylidyne) complexes during the course of their studies of the chemistry of the electron-rich allenylidenes $[Cp^*Ru(=C=C=C(R)Ph)(dippe)][BPh_4]$.[92]

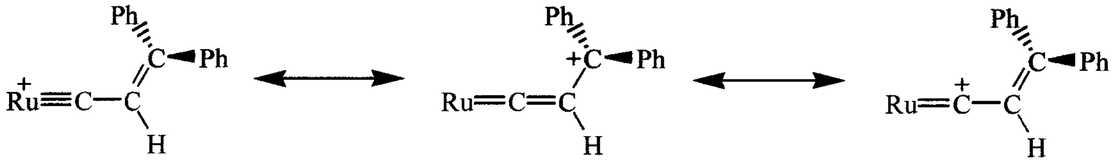
The preparations of the compounds in question are outlined in Scheme 39.



Scheme 39

The isomerization of the propargyl alcohols $HC{\equiv}CC(OH)(R)Ph$ into allenylidene moieties was effected by adding a slight excess of these to solutions of $Cp^*RuCl(dippe)$[93] and $Na[B(Ar^f)_4]$ in fluorobenzene, followed by a 3 hour stirring at room temperature to yield $[Cp^{*}Ru(=C=C=C(R)Ph)\text{-}(dippe)][B(Ar^{f})_4]$, **SM48.** Protonations were carried out by adding a slight excess of freshly prepared $[H(Et_2O)_2][B(Ar^{f})_4]$ to solutions of **SM48** in fluorobenzene while cooling with an $EtOH/N_2(\mathit{l})$ cold bath (−42 °C). The red solution is then warmed gradually to room temperature at which point the solvent is removed and the dark red products $[Cp^{*}Ru(\equiv CCH=C(R)Ph)(dippe)][B(Ar^{f})_4]_2$, **48** (R = H **a**, Ph **b**) are purified through washing with petroleum ether. Single crystals of **48b** (R = Ph) suitable for X-ray crystallographic analysis were also obtained via slow diffusion of petroleum ether into a solution of **48b** in Et_2O.

The NMR analysis of these complexes are understandably similar. The appearance of the ^1H NMR signals at δ 6.53 and 6.31 ppm for **48a** and **b**, respectively, correspond to the olefinic C_β protons. These values are similar to that observed with the similar complex $[CpOs(\equiv CCH=CPh_2)(P^iPr_3)_2][PF_6]$.[94] The values for the low-field C_α signals for **48a** and **48b** to δ 332.4 and 327.5 ppm, respectively, are well within the range for Ru-alkylidynes (see Table 4). One ^{13}C NMR signal trend observed with other Ru-vinyl(alkylidynes) that is shared with **48a** and **48b** is the higher $\delta(C\gamma)$ values, 167.9 and 180.1 ppm, relative to $\delta(C_\beta)$, 141 and 138.1 ppm, respectively (Section 1.4.2.5). However, the authors propose this to be the result of the involvement of a vinylidene resonance contributor that imposes a *positive* charge on $C\gamma$ (*i.e.* in contrast to that postulated by Fogg[90]). The X-ray structure, which proves that the structure of **48b** is in fact that of an Ru-alkylidyne, indicates that the Ru≡C bond length is among the longest of those that have been reported for this type of complex, being 1.766 Å (see Table 4). This structure also exhibits a similarity between the $C_\alpha - C_\beta$ and $C_\beta - C\gamma$ bond lengths (1.388 and 1.384 Å, respectively), which strongly supports the involvement of the different resonance contributors shown in Scheme 40.

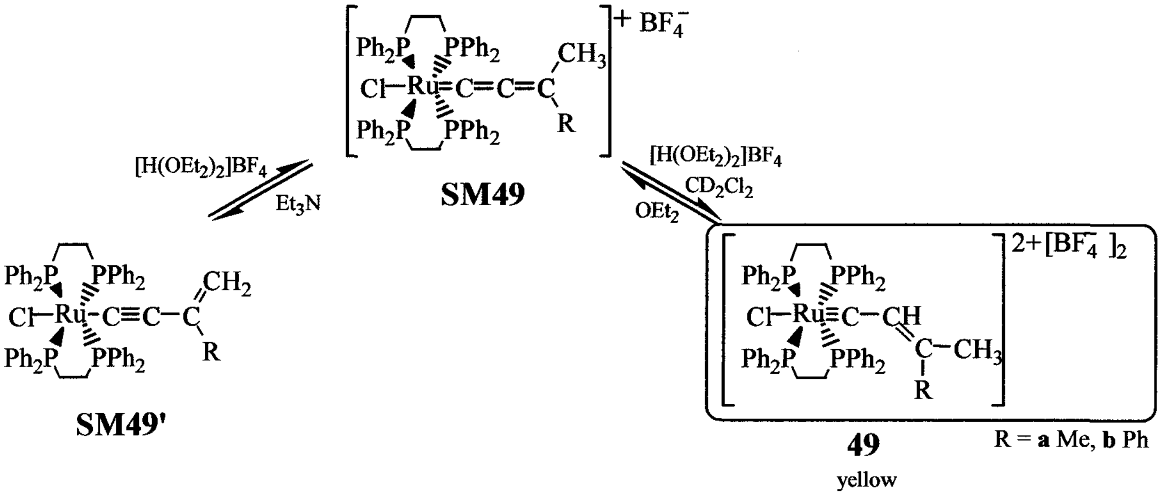


Scheme 40

Although there have been no investigations into the activity of **48** in olefin metathesis catalysis, it has been established that these compounds, which are moderately air-stable in the solid phase, are readily deprotonated by mildly basic agents such as methanol and acetone. **48a** has also been shown to undergo nucleophilic addition reactions with such agents as pyrazole and phenylsulfane. **48b**, however, is inert toward such reactions.

1.4.2.7 *Rigaut and Touchard's Dicationic Ruthenium Bis(diphosphino)vinyl(alkylidynes), $[RuCl(\equiv CCH{=}C(R)CH_3)(dppe)_2][BF_4]_2$*

In a continuation of the study on the amphoteric nature of *trans*-$[RuCl(=C=C=C(R)CH_3)\text{-}(dppe)_2][BF_4]$ complexes, **SM49**,[95,97] Rigaut and Touchard et al. explored in 2003[96] the products which may be obtained through reaction of such allenylidenes with acids and bases, the salient features of such procedures being outlined in Scheme 41.



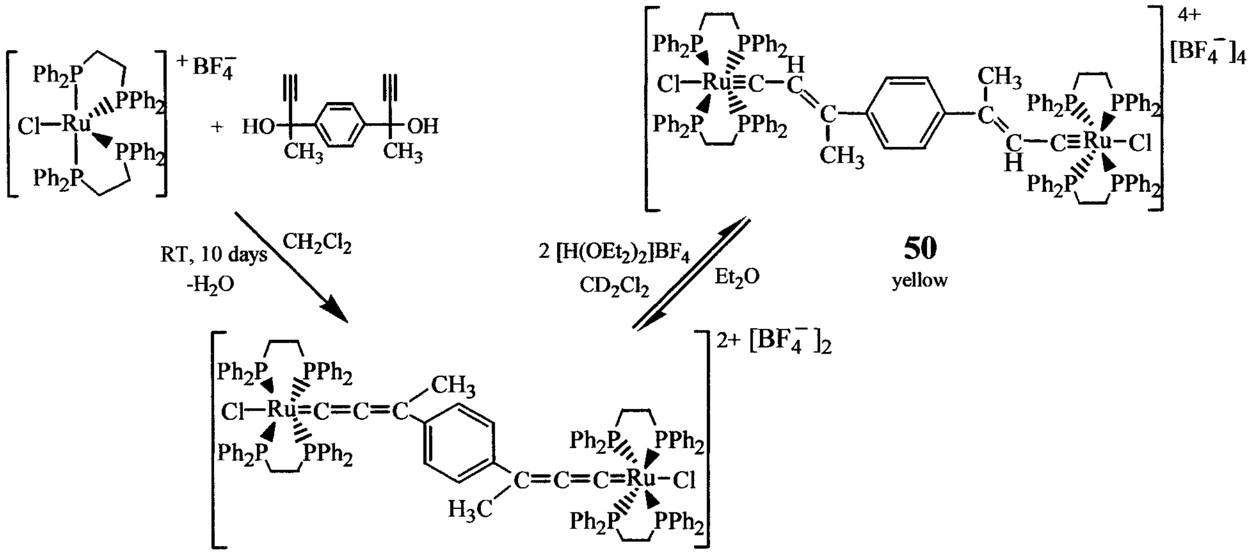
Scheme 41

They discovered that while the alkenyl acetylide complexes *trans*-$[RuCl(-C\equiv C-C(R)=CH_2)(dppe)_2]$, **SM49'**, may be obtained from treatment of methyl-substituted allenylidenes with the base NEt_3 in CH_2Cl_2 for 1 hour at room temperature, reaction of this new complex with equimolar $[H(Et_2O)_2][BF_4]$ gave back complexes **SM49** through reprotonation of the substituent methyl carbon. Furthermore, they also discovered, prompted by other recent examples (Sections 1.4.2.4 and 1.4.2.6), that protonation of **SM49** with excess $[H(Et_2O)_2][BF_4]$ (three equivalents) at room temperature in CD_2Cl_2 under NMR conditions yielded the yellow Ru-alkylidyne complexes *trans*-$[RuCl(\equiv CCH{=}C(R)CH_3)(dppe)_2][BF_4]_2$, **49**, (R = CH_3 **a**, Ph **b**), with the substantial excess of acid being necessary to force the equilibrium toward alkylidyne production. The C_β proton of the resulting alkylidyne is so acidic, in fact, that even the use of Et_2O in washing the crude products **49a** and **b** results in the regeneration of the corresponding **SM49** complex through deprotonation.

Characterization of **49**, like **46** and **48** before it, was effected through the use of ^1H and ^{13}C NMR spectroscopy. From ^1H NMR, analogous signals appear at δ 6.19 and 6.09 ppm, corresponding to the vinylic proton of **49a** and **b**, respectively. Interestingly, the two signals for the methyl protons of **49a** appear at very different positions, namely δ 1.68 and -0.11 ppm. The latter high-field signal is very unusual for methyl protons, but is rationalized by the authors to be the result of an increased shielding of these protons due to the likely close through-space proximity of the *cis* methyl group to the dppe ligands. The correlations between the aromatic protons of the dppe ligand and the protons of the methyl group, as well as between the vinylic carbon and the other methyl group, were also revealed through NOESY experiments.

From the ^{13}C NMR spectra, it was shown once again that these complexes adhere to the trend observed for the other vinyl(alkylidyne) complexes **46** and **48.** This trend involves the appearance of the **49a** and **b** signals for $C\gamma$, at δ 199.65 and 184.67 ppm, substantially downfield from those of C_β, at δ 129.94 and 125.45 ppm, respectively. This may be related to some resonance structure contributions as postulated for Valerga's vinyl(alkylidynes), but sadly the lack of X-ray structure characterization of **49** makes it difficult to state this conclusively as fact. The presence of the ^{13}C signals at δ 307.74 and 323.05 ppm, which correspond to C_α of **49a** and **b**, respectively, reinforces the fact that there has been some change in the environment of this carbon atom when compared to the parent allenylidenes.[95]

A novel bimetallic Ru-alkylidyne was also produced during this study. The preparation, as outlined in Scheme 42, entails the reaction of one equiv. of allenylidene complex *trans*-[*p*-$\{RuCl(dppe)_2(=C=C=C(CH_3)\}_2$-$C_6H_4][BF_4]_2$, **SM50**, with eight equiv. of $[H(Et_2O)_2][BF_4]$ in CD_2Cl_2 under NMR conditions to reveal the formation of the yellow bis-vinyl(alkylidyne) product *trans*-[*p*-$\{RuCl(dppe)_2(\equiv C-CH=C(CH_3)\}_2$-$C_6H_4][BF_4]_4$, **50**.



50
yellow

SM50

Scheme 42

The NMR analysis of the reaction mixture confirmed the presence of the desired compound. Due to the symmetry of this molecule and its similarity in structure to that of **49**, there is only one set of NMR data obtained for **50** due to the equivalence of analogous atoms. For instance, the signals at δ 6.10 and 0.39 ppm in the ^1H NMR spectrum correspond to the protons of both C_β and methyl substituents, respectively. Also, the ^{13}C NMR signals at δ 314.13, 182.35, and 128.41 ppm represent C_α, $C\gamma$, and C_β, respectively.

The authors also commented on the change in λ_{max} observed between **SM49** and **49** and **SM50** and **50**, as observed through UV-Vis spectral analysis of these compounds.

It was found that upon protonation, the metal-to-ligand-charge transfer band undergoes a significant blue shift (~60 nm) due the change in conjugation of the system that accompanies these protonations. Understandably, the observed blue shift is greater for the bimetallic alkylidyne **50** (~93 nm) compared to the monometallic complexes **49**.

1.4.3 *Other Compounds Containing Ruthenium-Carbon Triple Bonds*

In addition to these well-defined Ru-alkylidyne complexes, there have been other instances in which a Ru≡C bond has been observed, albeit in unusual forms.

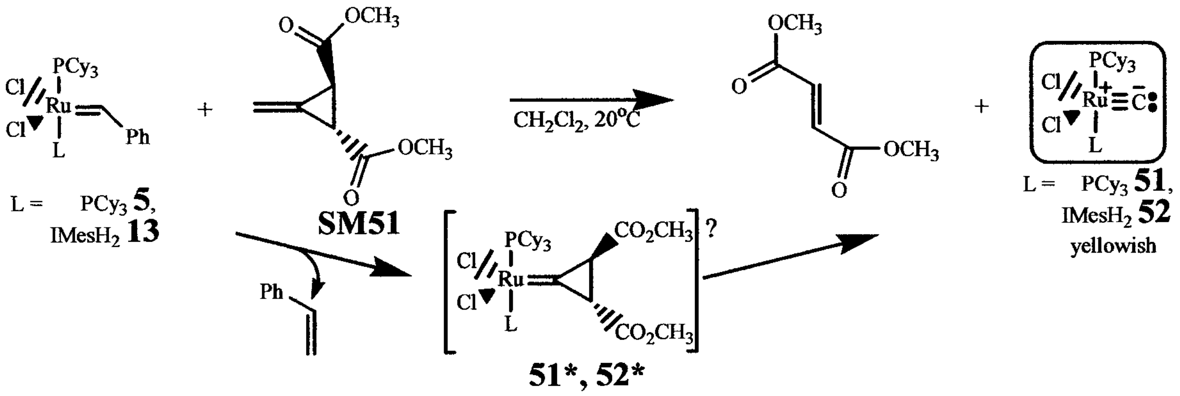
1.4.3.1 *Ruthenium-Carbide Complexes*

In a few recent isolated reports, complexes which were isolated from the reaction mixtures of Ru-alkylidene olefin metathesis processes were shown, after structural characterization through X-ray crystallization, to exhibit a single carbon atom triply-bonded to the Ru atom coordination centre.

The first examples of this was reported in 2002[98] by Heppert et al. as the result of an unusual olefin metathesis reaction involving the CM of a methylenecyclopropane substrate by either Grubbs'-catalyst $(PCy_3)_2Cl_2Ru{=}CHPh$, **5**, or it's $IMesH_2$-substituted derivative $(IMesH_2)(PCy_3)Cl_2Ru{=}CHPh$, **13**, the progression of which are illustrated in Scheme 43. Firstly, using **5** as the "catalyst", 2.5 equiv. of *trans*-2,3-dicarbomethoxymethylenecyclopropane, **SM51**, were reacted with **5** in CH_2Cl_2 at room temperature to yield the yellow product $(PCy_3)_2Cl_2Ru^+{\equiv}C^-$, **51**.

Similarly, the CM of excess (eight equiv.) **SM51** by **13** in CH_2Cl_2 at room temperature results in the production of the carbide product $(IMesH_2)(PCy_3)Cl_2Ru^+{\equiv}C^-$, **52**, in poor yield (20%). However, single crystals of **52** grown from benzene were suitable for analysis by X-ray crystallography.

The ^{13}C NMR analysis of **51** indicated the extreme situation of deshielding experienced by the carbon atom bonded to the Ru atom. This is illustrated by a

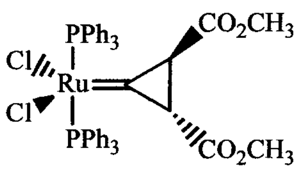


Scheme 43

extremely low-field singlet occurring at δ 471.5 ppm, which is certainly among the furthest down field signals ever reported for Ru–*C* species. Similarly, **52** exhibits even more deshielding of its carbide carbon with a ^{13}C NMR signal appearing at δ 479.64 ppm. Both of these complexes therefore exhibit signals in their ^{13}C NMR spectra similar to that of previously reported W- and Mo-based "carbides".[99]

The carbide nature of **51** and **52** is also supported by the X-ray crystal structure of **52**, which clearly indicates that the proposed carbide structures have been aptly assigned. The Ru≡C bond length of 1.650 Å is certainly among the closest associations of Ru and C atoms ever observed. An interesting observation derived from the X-ray structure is that the carbide carbon of **52** seems to be guarded by one of the mesityl rings of the IMes-H_2 and two of the PCy_3 Cy groups. This does well to rationalize the unexpected stability of **51** and **52** toward air and moisture when compared with other transition metal carbibes.[99]

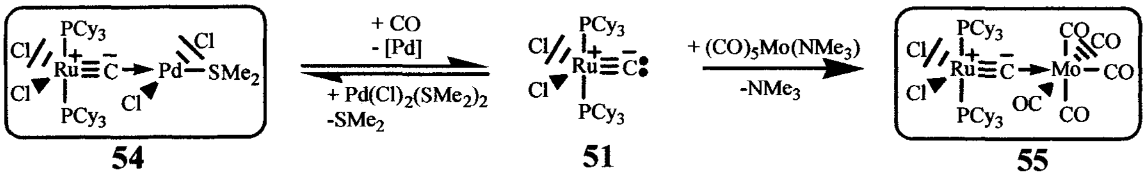
The mechanism through which these unusual complexes are prepared is thought to proceed through the involvement of alkylidene(cyclopropane) intermediates, **SM51*** and **SM52***, shown in Scheme 43. This theory, suggested by the authors, is based on the 2,3-dicarbomethoxycyclopropane alkylidene complex **53** reported by Grubbs *et al.* in 1995[100] and is rationalized through the consideration that the stabilization of the carbide species may require a condition of higher electron density on the metal atom, as would be the case using the strongly basic PCy_3 and



53

IMes-H_2 ligands as opposed to PPh_3. This lower ligand basicity may be the reason why **53** does not isomerize to the corresponding carbide complex. Later on in 2002,[101] Grubbs *et al.* provided strong evidence for this by obtaining **51** through reaction of **53** with two equiv. of PCy_3.

In addition to its structural novelty, **51** has found utility as a strongly σ-donating ligand in the formation of μ-carbido complexes, $(PCy_3)_2Cl_2Ru^+\equiv C^-\rightarrow PdCl_2(SMe_2)$, **54**, and $(PCy_3)_2Cl_2Ru^+\equiv C^-\rightarrow Mo(CO)_5$, **55**, as outlined in Scheme 44. The preparation of **54** was carried out through the simple stirring of **51** with a slight excess of $PdCl_2(SMe_2)_2$ in CH_2Cl_2 for 5 hours at room temperature. Removal of the solvent and recystallization from benzene/hexanes yielded the desired pale yellow product **54**. Conversely, **55** was identified *in situ* through reaction of **51** with a slight excess of $(CO)_5Mo(NMe_3)$ in CD_2Cl_2 with 6 hours of tumbling at room temperature in a screw-cap NMR tube.

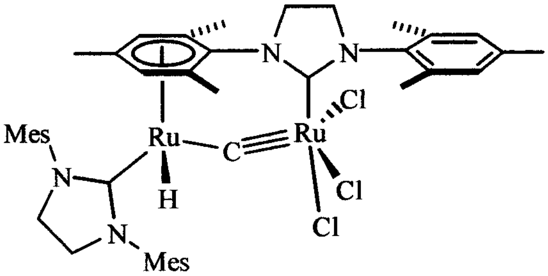


Scheme 44

The ^{13}C NMR spectra of **54** and **55** revealed the unmistakable low-field signals at δ 381.2 and 446.3 ppm, respectively, which obviously correspond to the μ-carbido C atoms.[101,102] The authors speculate that the greater observed decrease in the δ-value of **54** relative to **55**, when compared to that of the uncoordinated **51**, suggests that there may be a weaker bonding interaction between the carbide ligand and Mo atom as opposed to with the Pd atom.

X-ray crystal structures were solved for both **54** and **51**. Firstly, the Ru≡C bond length of **51**, at 1.632 Å, is even shorter than that of **52**. Although the coordination of **51** to the Pd atom of $PdCl_2(SMe_2)_2$ results in a lengthening of this bond length (to 1.662 Å), this is still found to be comparable to other Ru-alkylidynes (Section 1.4.2.2). For this reason, the authors label the Ru−C interaction as a triple bond and the C−Pd interaction as a single bond. Also, the slight lengthening of the bond between the Pd and S atoms of the SMe_2 group *trans* to the carbido carbon (*i.e.* from 2.319 to 2.356 Å) is taken by the authors to indicate the stronger *trans*-influence of ligand **51** compared to that of the displaced SMe_2 ligand.

Aside from the above deliberate preparations of Ru-carbide species, there has also been reported a biruthenium μ-carbido complex **56.** It seems that Grubbs et al. in 2004,[103] while trying to identify the decomposition products of the olefin metathesis intermediate (IMes-H_2)$RuCl_2$-(=CH_2)(PCy_3),[104] **13**, obtained **56** from heating a solution of **13** in benzene to 55 °C for 72 hours as an orange-yellow crystalline solid.



56

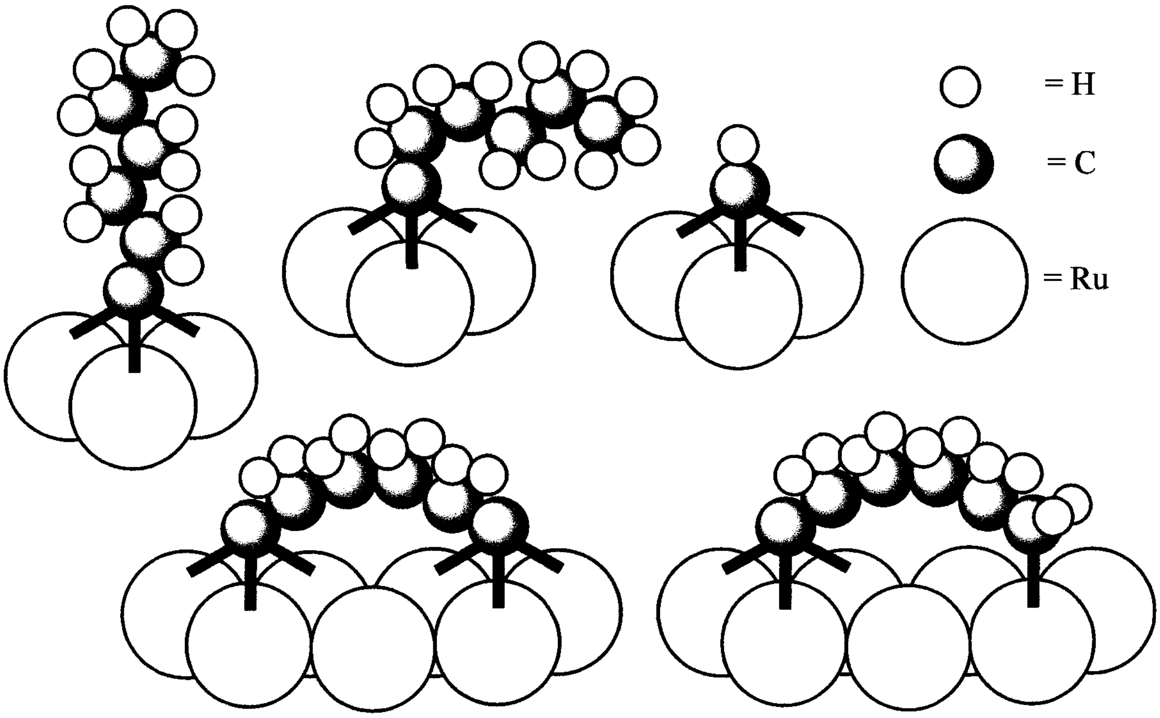
Both ^{13}C NMR and X-ray crystallographic analyses were carried out on **56.** The ^{13}C signal at δ 414.0 ppm is similar to that of the aforementioned Ru-carbide complexes and is within the range expected for μ-carbido species.[101,102] Upon scrutiny of the X-ray structure, however, there is some doubt as to the true identity of the "μ-carbido" moeity. The observed similarity between the $Ru\equiv C$ and $Ru-C$ bond lengths of 1.698 and 1.875 Å, respectively, suggests the possibility that the real identity of **56** might include an allylidene species [Ru=C=Ru]. This theory was discarded by the authors upon the realization that such a structure would result in involved Ru atoms having electron counts of 15- and 19-electrons, which is not likely to occur.

An interesting discovery concerning **56** is the observation that this complex catalyzes the isomerization of olefins under conditions similar to those of olefin metathesis. This is an important revelation since the hitherto unknown species responsible for this undesirable side-reaction of olefin metathesis may therefore be similar in structure to **56.**

1.4.3.2 *Alkylidyne Species on Ru (0001) Surfaces*

The formation of surface-bound alkylidyne species has been observed to result from the thermal decomposition of chemically adsorbed species on Ru(0001) surfaces.[105]

In a recent example, Ilharco et al. investigated the adsorption and thermal decomposition of 1-hexyne on single crystal Ru(0001) surfaces in 2002.[106] Based on Reflective-Absorption InfraRed Spectroscopy (RAIRS) data, it was observed that at low temperatures (92 K), 1-hexyne may be adsorbed (*i.e.* adsorption causing changes in chemical bonding of molecule) to the metal surface as a di-σ/π complex, which involves the interaction of the two alkynyl C atoms with two separate Ru atoms in a σ-fashion, as well the interaction of the C–C multiple bond in a π-fashion. Upon annealing of the sample to 120 K, there is observed the formation of a hexylidyne species which may assume different conformations based on the temperature and adsorbant exposure. At higher temperatures, it seems that the *gauche* conformation, with the terminal methyl group facing toward the metal surface, is the predominant conformer, as is also the case for 1-hexene on Ru(0001).[107] This conformation becomes understandable when considering the observation that after annealing the sample at 280 K, a new intermediate is observed which is assignable to a metallocycle formed upon partial dehydrogenation of the hexylidyne species. At 290 K, this species undergoes a more complete dehydrogenation to form the bis(alkylidyne)metallacycle, a process which is also observed with the decomposition of hexylidyne species on Pt(111) surfaces.[108] The common thermal methylidyne decomposition product[109] is also observed at 280 K and becomes the only detectable surface species after 300 K. The bonding modes of these various alkylidyne species are illustrated in Scheme 45.



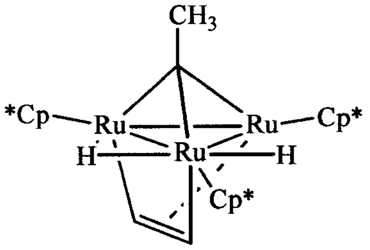
Scheme 45

1.4.3.3 *Triruthenium Alkylidyne Clusters*

As an intermediate class to solution-characterized and solid-state-characterized metal alkylidynes, the development of Ru-based cluster species which incorporate alkylidyne moeities has also been undertaken. Like surface-bound alkylidynes (Section *1.4.3.2*), alkylidyne clusters also exhibit the μ_3-bonding convention, with the alkylidyne carbon atom being bonded to three different metal atoms.

In the recent literature, there are relatively few reports of purely homometallic Ru-alkylidyne cluster species. Among the most recent examples of these is the μ_3-ethylidyne- μ_3-$\eta^2(\|)$-ethyne cluster $(\mathrm{Cp^*Ru})_3(\mu\text{-H})_2(\mu_3\text{-CCH}_3)\{\mu_3\text{-}\eta^2(\|)\text{-CH=CH}\}$, **57**, introduced by Suzuki et al. in 2002.[110] The rapid continuation of this work by Suzuki et al. in 2003 showcased the μ_3-methylidyne- μ_3-diruthenaallyl cluster complex $(\mathrm{Cp^*Ru})_3(\mu$-

H)(μ_3-CH)[μ_3-C(R)C(Me)CH], **58**,[111] (R = H **a**, CH_3 **b**).



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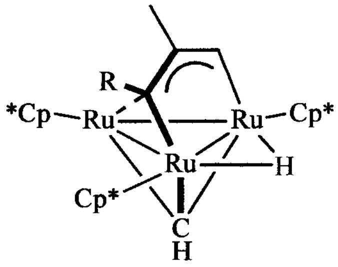
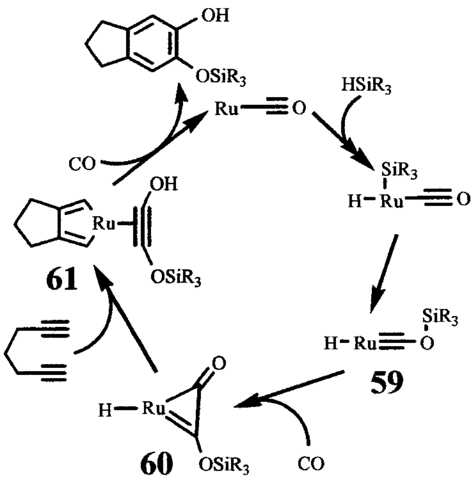


58

1.4.3.4 *Ruthenium Alkylidyne Intermediate in Catechol Production*

Work published by Murai <u>et al.</u> in 1993[112] indicates that an oxycarbyne complex **59** serves as an intermediate in the reaction between 1,6-diynes, hydrosilanes and CO to produce catechol species. The catalytic cycle proposed by the authors, as illustrated in Scheme 46, finds support in the following accounts. Based on studies with W-based systems,[113,121] the involvement of an oxycarbyne intermediate en route to the corresponding oxyacetylene complex, similar to **61**, has been shown to include a similar intermediate to **60.** Also, observation of a similar product from the reaction of 1,6-diynes with the carbonyl(ethylidyne) complexes $(CO)_4BrM{\equiv}CCH_3$ (M = Cr, W) reported by Katz in 1985[114] lends great credibility to the mechanism proposed by Murai.



Scheme 46

1.5 Electrophilic Attack Reactions Resulting in Alkylidyne Production

In reviewing the above discussions of Ru-alkylidyne production, it should be clear that the safest and simplest methods of alkylidyne production involve the electrophilic attack of Ru-vinylidene starting materials by H^+ (Section 1.4.2). In order to effectively design new alkylidyne complexes from vinylidene starting materials, it is helpful to explore both the theory and implementation of electrophilic attack reactions of vinylidenes.

1.5.1 *Theoretical Considerations*

In an attempt to quantify the probable reactivity patterns of vinylidene complexes toward electrophilic agents, Fenske et al. in 1982[115] published a molecular orbital treatment concerning various vinylidene-containing metal fragments using the nonparameterized Fenske-Hall self-consistent field (SCF) method.[116] This method is entirely dependant both on the molecular geometries of the species in question (*i.e.*, as obtained from X-ray crystal structures) and the basis functions of the molecular orbitals.

The results of these studies indicate that late transition metal vinylidene ligands were generally predicted to undergo C_α-additions by nucleophiles and C_β-additions by electrophiles. These predictions were made based on the observation that the electrophilic LUMO is typically centred on C_α, while the charge distribution of the nucleophilic HOMO imposes a slight negative charge at C_β which seems to control the addition of electrophiles.

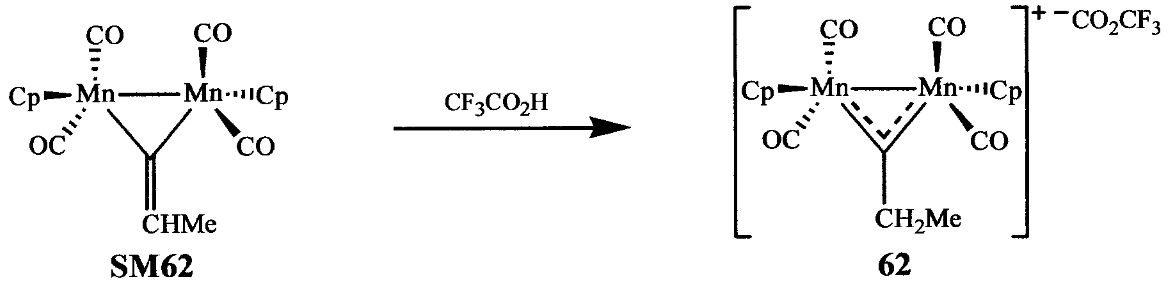
Also observed was the fact that while cationic complexes are understandably less reactive toward electrophilic attack, the regioselectivity of such reactions is maintained, since this is in every case determined by the distribution of electron density. This distribution was approximated by the authors using Mulliken population analysis.[116,117]

In similar studies by Gimeno[118] in 1996 and Esteruelas[119] in 1997, it was predicted through the use of Extended Huckel Theory Molecular Orbital calculations that electrophilic additions to Ru-allenylidenes should only occur at C_β. Again, this is based on the observation that the larger portion of the nucleophilic HOMO is centralized on this atom.

1.5.2 *Electrophilic Attack Reactions on Vinylidenes*

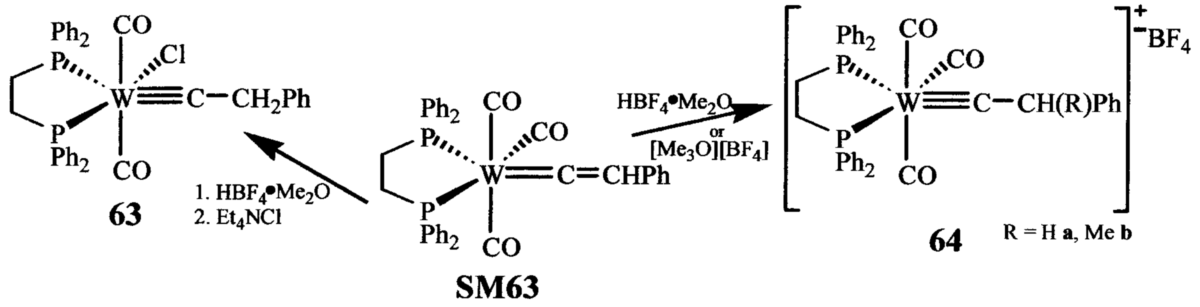
The account of Fenske et al. (Section 1.5.1) has served as the herald of well-planned deliberate electrophilic addition reactions of vinylidenes. In the context of alkylidyne production, several reports have exhibited the C_β-attack of vinylidene moeities by H^+, as well as a few that utilize alkyl cations as the electrophile. These reactions are illustrated in Schemes 47 a-e.

It should be mentioned at this point that one of the first research groups to postulate that electrophilic additions to vinylidene ligands may result in alkylidyne species was Caulton et al. in 1980.[120] This hypothesis was based on the observation by the authors that treatment of the dimanganese(vinylidene) complex $\{CpMn(CO)_2\}_2(\mu_2$-η^1-CH=CHR), **SM62**[120] (R = H, Me), with CF_3CO_2H afforded the alkylidyne product $[\{CpMn(CO)_2\}_2(\mu_2\text{-C-}CH_2R)]CF_3CO_2$, **62**, (Scheme 47a). Most peculiar to the authors was the revelation that while most alkylidynes up to that point were produced through the abstraction of groups from C_α of some ligand,[121] this work involved the addition of groups to coordinated species.



Scheme 47a

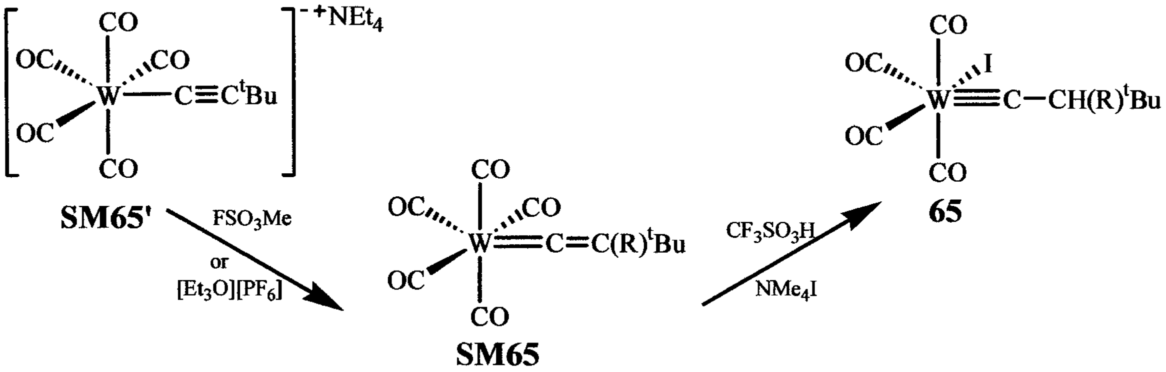
Shortly after Fenske's account[115] there was reported experimental findings by Templeton et al. in 1983[122] that demonstrates the accuracy of this theory. The simple preparation and treatment of the vinylidene *mer*-W(CO)$_3$(dppe)(=C=CHR), **SM63** (R = CO$_2$Me, C$_6$H$_5$), with HBF$_4$•Me$_2$O followed by addition of [NEt$_4$]Cl resulted in the protonation of C_β and the formation of the alkylidyne product *mer*-W(CO)$_2$Cl(dppe)-(≡C−CH$_2$R), **63**, (Scheme 47b). Later on in 1985,[123] this same group reported the use of the electrophiles HBF$_4$•Me$_2$O and [Me$_3$O][BF$_4$] to convert **SM63** into halide-free alkylidynes [*mer*-W(CO)$_3$(dppe)(≡C−CH$_2$R)][BF$_4$], **64** (R = H **a**, Me **b**), simply by leaving out the [NEt$_4$]Cl-treatment step.



Scheme 47b

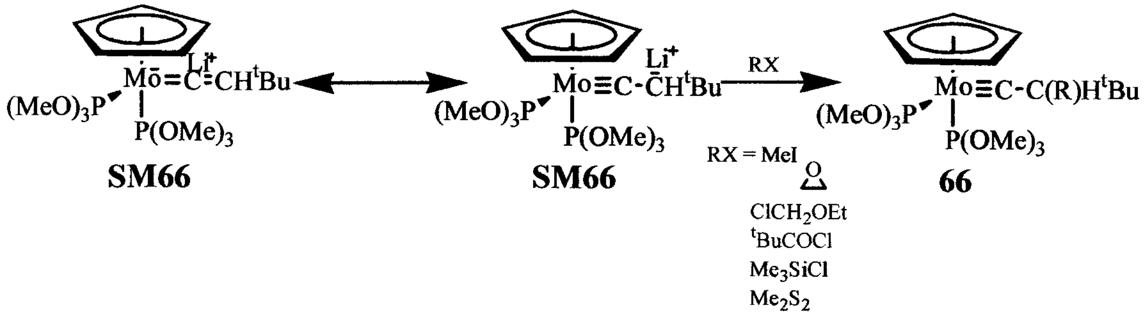
Work by Mayr _et al._ in 1984[124] involved the publication of alkylidyne production methods through double electrophilic addition reactions to C_β of acetylide ligands. This study involved the use of alkylating agents such as FSO_3Me or $[Et_3O][PF_6]$ to convert the acetylide $[NEt_4][(CO)_5W(C{\equiv}C^tBu)]$, **SM65'**,[125] to the vinylidene $(CO)_5W(=C=C(R)^tBu)$, **SM65** (R = Me **a**, Et **b**), which then undergoes C_β-protonation by CF_3SO_3H in the presence of NMe_4I to yield $I(CO)_4W({\equiv}C-CH(R)^tBu)$, **65** (R = Me **a**, Et **b**) (Scheme 47c).

In 1985, one research group demonstrated the utility of several different alkylating agents in electrophilic addition reactions to the novel anionic lithium molybdenum(vinylidene) complex $Li[Mo(=C=CH^tBu)\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5)]$, **SM66**.[126] As Scheme 47d implies, this reaction is simply an example of trapping an alkylidyne resonance contributor $[CpMo\{P(OMe)_3\}_2({\equiv}C-C(R)H^tBu)]$, **66**, using alkyl electrophiles.



Scheme 47c

In two separate publications in 1988,[127] Pombeiro _et al._ demontrated the



Scheme 47d

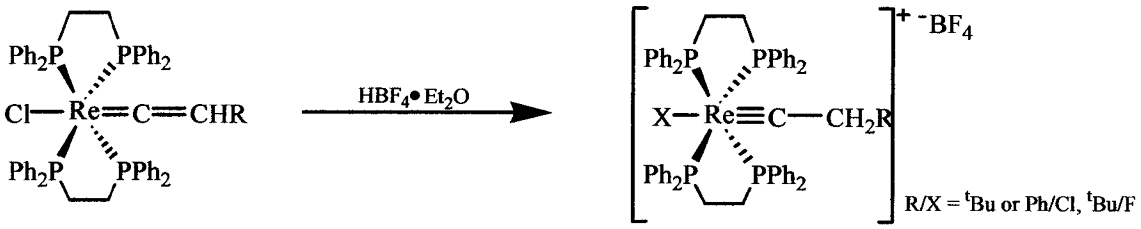
production of alkylidynes from vinylidenes[127a] and acetylides.[127b] In the first article, the protonation of $WH_2(-C{\equiv}CH_2CO_2Me)_2(dppe)_2$, **SM67**, with $HBF_4{\bullet}Et_2O$ leads to the formation of $WF({\equiv}C-CH_2CO_2Me)(dppe)_2$, **67** (Scheme 47e).

SM67 **67**

Scheme 47e

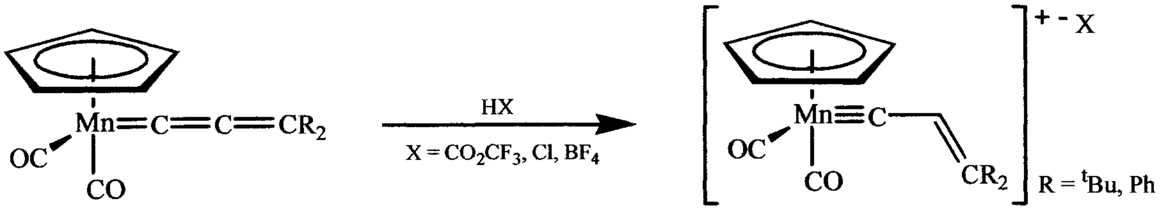
In the second communication, it was shown that the use of $HBF_4{\bullet}Et_2O$ in the protonation of *trans*-[ReCl(=C=CHR)(dppe)$_2$], **SM68**, yields a mixture of the alkylidyne complexes *trans*-[$ReX({\equiv}C-CH_2R)(dppe)_2$][$BF_4$], **68** (R/X = ^{t}Bu or Ph/Cl, ^{t}Bu/F), as shown in Scheme 47f. The incorporation of F into the complexes is thought by the authors to result from the function of the BF_4^- as a metal fluorinating agent.

For a final example of this type of reaction, we glance briefly at an electrophilic addition reaction of an allenylidene. Electrophilic additions were mentioned earlier to occur preferentially at C_β, a fact alluded to in Section 1.5.1. In addition to the instances of protonation of Ru-allenylidenes given in Section 1.4.2., there has also been reported the addition of HX (X = CF_3CO_2, Cl, BF_4) to the allenylidene $Cp(CO)_2Mn{=}C{=}C{=}CR_2$, **SM69** (R = ^{t}Bu, Ph), to give the vinyl(alkylidyne) [$Cp(CO)_2Mn{\equiv}C-CH{=}CR_2$]X, **69**, as reported by Kolobova et al. in 1984 (Scheme 48).[128]



SM68 **68**

Scheme 47f



SM69 **69**

Scheme 48

Upon consideration of the above material, it becomes apparent that although there is a wealth of knowledge available concerning both the metathesis of alkyne substrates using early transition metal catalysts and the synthesis of Ru-alkylidyne complexes, there has yet to be reported a Ru-based species that exhibits alkyne metathesis activity. Therefore, the focus of this research project is the synthesis of new Ru-alkylidyne complexes and the attempted application of these to alkyne metathesis.

1.6 Introduction References

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2. Research Proposal

In considering the above review of olefin and alkyne metathesis processes and catalysts in Sections 1.1 through 1.4.1.4, as well as the consideration of the various Ru-species known to possess alkylidyne moeities presented in Sections 1.4.2 through 1.4.3.4, there are several core themes which are ubiquitous.

For example, the higher electron-density of the late transition metal Ru versus traditional early transition metals (*i.e.* Mo, W) serves to stabilize an olefin metathesis catalyst towards a variety of functional groups present on potential substrates. This raises the question of whether an alkylidyne complex based on Ru would exhibit the same tolerance towards functionalized alkyne substrates. Therefore, this project is focussed centrally on the synthesis of new Ru-alkylidynes while keeping the potential for application to alkyne metathesis processes in mind.

Also apparent is the requirement that these complexes have a readily dissociable ligand included in the construction of precatalyst species based on Ru. Traditionally, this role has been fulfilled by the neutral and strongly σ-donating/weakly π-accepting phosphine ligands. Since the incentive for phosphine dissociation can be largely affected by steric factors, it is reasonable to assume that the use of sterically demanding, relatively nonlabile ancillary ligands would facilitate dissociation. In addition, large chelating ancillary ligands serve the dual purpose of locking the geometric configuration around the metal while in most cases providing the steric influence required for forcible dissociation of labile species. It is for these reasons that the complexes studied in this project will include $C_5Me_5^-$ (*i.e.* "Cp*") and $HB(pz)_3^-$ (*i.e.* "Tp", pz = 2-pyrazolyl) ligands as they are well known sterically-demanding species.[1]

As mentioned in Section 1.4.2.2, the preparation of Ru-alkylidyne complexes through C_β- protonation of appropriate Ru-vinylidene starting materials has proven itself to be a convenient and efficient method for producing these species in high yields. The attack of the vinylidene ligand at C_β is also the predicted pathway for this electrophilic addition reaction as shown by Fenske et al. (Section 1.5.1). Another advantage of this experimental strategy is the ease with which many Ru-vinylidenes may be prepared. The use of neutral Ru-vinylidene complexes is the preferred course of action in this project as they would yield monocationic alkylidynes upon protonation as opposed to the relatively more abundant cationic Ru-vinylidenes, which would yield dicationic alkylidynes. This underscores the importance of the large volume of research conducted towards the development of convenient methods for synthesis of these neutral materials. Having all of the above points in mind, it is therefore the focus of this project to prepare new Ru-alkylidynes through protonation of readily available Ru-vinylidene starting materials which incorporate the bulky polydentate ligands Cp^* and Tp.

The vinylidene starting materials used during this study ideally will also include a variety of functional groups on C_β of the vinylidene ligand. As observed by Werner et al. on Ru-vinylidene protonation (Section 1.4.2.2),[2] it is to be expected that the identity of this functional group is likely to exert a some influence on the stability of the resulting alkylidyne species.

In addition to these protonation studies, the electrophilic addition reactions to the neutral vinylidene starting materials will be extended to include other electrophiles. One particular and readily available candidate is Me^+, of which MeOTf may serve as a source. While the synthesis of a Ru-methyl(alkylidyne) via MeOTf treatment of the corresponding Ru-vinylidene has never been reported, there is precedent for this concerning the C_β-methylation of W-vinylidenes with $[Me_3O][BF_4]$ provided by Templeton et al. (Section 1.5.2).[3] Once again, the attack of the vinylidene ligands by the methyl cations at C_β was previously predicted by Fenske et al. (Section 1.5.1).[4]

Finally, alkylidynes synthesized during these studies will undergo preliminary application studies for use in alkyne metathesis processes provided the stability of said complexes is sufficient.

2.1 Proposal References

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3. Experimental

General Considerations:

The experiments described below were all carried out under an inert atmosphere of prepurified N_2 using standard Schlenk line procedures unless otherwise indicated. EtOH, MeOH and DMF were dried over activated 4 Å molecular sieves and rigorously degassed with a stream of Ar, then stored under N_2 in round bottom storage bottles fitted with Teflon taps. All other solvents used during reactions were rigorously dried with appropriate drying agents (CH_2Cl_2: CaH_2; Et_2O, benzene, toluene, THF and hexanes: Na/benzophenone) and distilled prior to use. The dispensing of solvents was carried out using syringes. All non-room temperature reaction mixtures were either heated using oil baths or cooled using acetone/N_2(*l*) cold baths as required. The drying and degassing of NMR solvents involved stirring the bottled solvent with an appropriate drying agent ($CDCl_3$: $CaCl_2$; CD_2Cl_2: CaH_2; C_6D_6: Na metal) followed by vacuum distillation and a threefold freeze-pump-thaw degassing practice, at which point the solvents were stored under N_2 in round-bottom bulbs with Teflon taps. All NMR data (^1H, ^{31}P, ^{13}C, and ^{19}F) were acquired through the use of a Varian Unity INOVA 500 MHz spectrometer, with sample chemical shifts in ppm referenced to residual protio solvent peaks (^1H), TMS (^{13}C), external 85% H_3PO_4 (^{31}P), and external $CFCl_3$ (^{19}F). Elemental analyses were performed using a CEC 240XA analyser by the Lakehead University Instrumentation Laboratory (LUIL). All solid starting materials were prepared using literature procedures as referenced throughout this section and were stored as solids under conditions of dynamic vacuum. Solid $RuCl_3 \bullet xH_2O$ was purchased from Pressure Chemicals. All other solid reagents were purchased from Aldrich, were stored under dry conditions and used without further purification. All liquid reagents (*i.e.* alkynes, Cp^*H, MeOTf, HBF_4/Et_2O solution) were also purchased from Aldrich, and used as received.

Synthesis of $[Cp^*RuCl(=C=CH(^nBu))(PPh_3)]$, 70b.

0.301 g (0.379 mmol) of $[Cp^*RuCl(PPh_3)_2]$[3] were dissolved in 30 mL benzene. The resulting orange solution was stirred at room temperature while 5 molar equivalents of $HC{\equiv}C^nBu$ (217 μL, 1.895 mmol) were added via syringe. The reaction mixture was then heated to reflux and stirred for 30 min. A colour change from orange to deep red was observed after 15 min. Upon completion, the reaction mixture was cooled to room temperature and the volatiles were removed under reduced pressure. Purification of **70b** was effected through slow diffusion of MeOH into a solution of **70b** in CH_2Cl_2. Yield = 0.133 g (56%). Anal. Calcd. for $C_{34}H_{40}ClPRu$: C, 66.26; H, 6.56. Found: C, 66.32; H, 6.81. ^{1}H NMR (499.9 MHz, $CDCl_3$, 22 °C): δ 8.00–7.00 (m, 15 H, Ph), 3.57 (t, 1 H, $^2J_{HH}$ = 7.3 Hz, Ru=C=C*H*), 2.07, (m, 2 H, Ru=C=CH(^{n}*Bu*)), 1.45 (d, 15 H, $^4J_{PC}$ = 1.5 Hz, $C_5(CH_3)_5$), 1.16 (m, 2 H, Ru=C=CH(^{n}*Bu*)), 1.01 (m, 2 H, Ru=C=CH(^{n}*Bu*)), 0.79 (t, 3 H, $^3J_{HH}$ = 7.3 Hz, Ru=C=CH(^{n}*Bu*)). $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$, 22 °C): δ 334.7 (d, $^2J_{PC}$ = 24.4 Hz, Ru=*C*), 135.0–127.7 (s, Ph), 106.8 (s, Ru=C=*C*H(^{n}Bu)), 100.8 (s, $C_5(CH_3)_5$), 33.94–13.96 (s, ^{n}*Bu*), 9.58 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ NMR (202.3 MHz, $CDCl_3$, 22 °C): δ 50.9 (s, *P*Ph$_3$).

Variable Temperature NMR Experiments: Reaction of 70a,b with HBF_4.

These experiments adhered to the general protocol described herein. A sample of either **70a** or **b** (~40 mg) was dissolved in 0.4 mL CD_2Cl_2 in a 5 mm NMR tube fitted with a rubber septum and attached to a N_2 line. The resultant red solutions were then cooled to −78 °C and treated with a slight excess of 54 wt% solution of HBF_4 in Et_2O (~1.2 molar equivalents) via syringe causing an immediate colour change from red to orange. The sample tube was then transferred to a precooled (−75 °C) NMR probe and data were acquired immediately. At this temperature, ^{1}H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR data were identical to that recorded for the corresponding $B(Ar^f)_4$ salts **72a** or **b** at −75 °C and unequivocally signified the quantitative formation of **71a** or **b**. No significant changes in the NMR spectra were observed between −75 °C and 22 °C.

Attempted C_{β}-methylation of 70a,b.

These experiments adhered to the following general protocol. A sample of either **70a** or **b** (~30mg) was dissolved in 0.4 mL CD_2Cl_2 in a 5 mm NMR tube fitted with a rubber septum and attached to a N_2 line. The resultant red solutions were then cooled to −78 °C and treated with 1 molar equivalent of neat MeOTf followed by gradual warming to room temperature. A colour change from deep red to dark brown with concomitant precipitation of a brown solid was observed. From $^{31}P\{^1H\}$ NMR analysis, it was revealed that the consumption of the vinylidenes **70a** and **b** reached completion after ~3 hrs. to give rise to several other unidentified species. Scrutiny of acquired ^1H NMR spectra revealed that the abstraction of a chloride ligand had occurred by the immediate presence of 1 molar equivalent of MeCl at δ ~3.0 ppm. $^{13}C\{^1H\}$ NMR analysis of old (~3 hrs.) reaction mixtures of both **70a** and **b** resulted in the observation of unidentified downfield triplets: **70 a,** δ 348.2 ppm (t, $^2J_{PC}$ = 14.5 Hz); **70b,** δ 349.7 ppm (t, $^2J_{PC}$ = 15.3 Hz).

Synthesis of $[Cp^*RuCl(\equiv C-CH_2(^tBu))(PPh_3)][BF_4]$, 71a.

0.223 g (0.362 mmol) of $Cp^*RuCl(=C=CH^tBu)(PPh_3)$[1] **70a** were dissolved in 3 mL CH_2Cl_2 and cooled to −78 °C. To the cooled deep red solution was added a slight excess of HBF_4 in Et_2O (55 μL of 54 wt% solution, 0.399 mmol) followed by stirring at this temperature for ~10 min. An immediate colour change from red to orange-brown was observed. The gradual warming of the solution to room temperature (~30 min) was followed by immediate removal of solvents under reduced pressure and washing of the resultant orange residue with 4 × 5 mL Et_2O. ^1H and $^{31}P\{^1H\}$ NMR analysis of the dried product revealed the quantitative formation of the alkylidyne species $[Cp^*RuCl(\equiv C-CH_2(^tBu))(PPh_3)][BF_4]$ **71a.** However, all attempts at growing single crystals of **71a** were frustrated by the high solubility of this complex. Yield: 0.229 g (90%). ^{1}H NMR (499.9 MHz, CD_2Cl_2, 22 °C): δ 7.79–7.30 (m, 15 H, P*Ph$_3$*), 3.11 (dd, 1 H, $^2J_{HH}$ = 20.3 Hz, $^4J_{PH}$ = 1.1 Hz, Ru≡CC*H*$_a$H$_b$(^{t}Bu)), 1.86 (dd, 1 H, $^2J_{HH}$ = 20.3 Hz, $^4J_{PH}$ = 3 Hz, Ru≡CCH$_a$*H*$_b$(^{t}Bu)), 1.65 (d, 15 H, $^4J_{PH}$ = 2 Hz, $C_5(CH_3)_5$), 0.97 (s, 9 H, $C(CH_3)_3$). ^{13}C{^{1}H} (125.7 MHz, CD_2Cl_2, 22 °C): δ 351.0 (d, $^2J_{PC}$ = 15.7 Hz, Ru≡*C*),134.8–129.3 (s, Ph), 110.5 (s, *C*$_5$(CH$_3$)$_5$), 67.4 (s, Ru≡C*C*H$_2$(^{t}Bu)), 36.6 (s, *C*Me$_3$), 30.4 (s, C(*C*H$_3$)$_3$), 10.0 (s, C$_5$(*C*H$_3$)$_5$). ^{31}P{^{1}H} NMR (202.3 MHz, CD_2Cl_2, 22 °C): δ 39.0 (s, *P*Ph$_3$).

Reaction of 71a with KO^{t}Bu.

0.0382 g (0.05426 mmol) of **71a** were dissolved in 0.3 mL of CD_2Cl_2 in a 5 mm NMR tube fitted with a rubber septum and attached to a N_2 line. 27 μL of a 1.0 M solution of KO^{t}Bu (0.027 mmol, 0.5 equivalents) in THF were added to the sample at room temperature with the production of a small amount of white solid and an immediate colour change from orange-brown to deep red. Analysis of the sample using both ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR indicated the near equal presence of both the alkylidyne **71a** and vinylidene species **70a** (based on ^{31}P{^{1}H} NMR spectrum integrations) along with a small amount of other unidentified compounds.

Synthesis of [Cp*RuCl(≡C–CH$_2$(^{n}Bu))(PPh$_3$)][BF$_4$], 71b.

0.194 g (0.314 mmol) of **70b** were dissolved in 3 mL CH_2Cl_2 and cooled to −78 °C. To the cooled deep red solution was added a slight excess of HBF_4 in Et_2O (56 μL of 54 wt% solution, 0.407 mmol) followed by stirring at this temperature for ~10 min. A colour change from red to orange-brown was observed. The gradual warming of the solution to room temperature (~30 min) was followed by immediate removal of solvents under reduced pressure and washing of the resultant orange residue with 4 × 5 mL Et_2O. ^{1}H and ^{31}P{^{1}H} NMR analysis of the dried product revealed the quantitative formation of the alkylidyne species [Cp*RuCl(≡C–CH$_2$(^{n}Bu))(PPh$_3$)][BF$_4$] **71b**. All attempts at growing single crystals of **71b** were frustrated by the high solubility of this complex. Yield: 0.195 g (88%). ^{1}H NMR (499.9 MHz, CD_2Cl_2, 22 °C): δ 7.66–7.39 (m, 27 H, Ph and $C_6H_3(CF_3)_2$), 2.35 (m, 1 H, $^2J_{HH}$ = 20.5 Hz, Ru≡CCH_aH$_b$(^{n}Bu)), 1.86 (m, 1 H, $^2J_{HH}$ = 20.5 Hz, Ru≡CCH$_a$$H_b$(^{n}Bu)), 1.56 (d, 15 H, $^4J_{PH}$ = 1.9 Hz, $C_5(CH_3)_5$), 1.48–1.09 (m, 6 H, Ru≡CH$_2$(^{n}*Bu*)), 0.77 (t, 3 H, $^3J_{HH}$ = 7 Hz, Ru≡CCH$_2$(^{n}*Bu*)). ^{13}C{^{1}H} (125.7 MHz, CD_2Cl_2, 22 °C): δ 349.4 (d, $^2J_{PC}$ = 17.1 Hz, Ru≡*C*), 135.8–129.2 (s, Ph), 110.6 (s, $C_5(CH_3)_5$), 66.1 (s, Ru≡*C*CH$_2$(^{n}Bu)), 31.6 (s, ^{n}Bu), 24.3 (s, ^{n}Bu), 22.2 (s, ^{n}Bu), 13.7 (s, ^{n}Bu), 10.0 (s, $C_5(CH_3)_5$). ^{19}F{^{1}H} NMR (470.2 MHz, CD_2Cl_2, 22 °C): δ -63.2 (s, CF_3 of Ar^f). ^{31}P{^{1}H} NMR (202.3 MHz, CD_2Cl_2, 22 °C): δ 38.6 (s, *P*Ph$_3$).

Reaction of 71b with NEt_3 and PPh_3.

NEt_3: 0.0086 g (0.0122 mmol) of **71b** were dissolved in 0.5 mL $CDCl_3$ in an NMR tube under N_2. 4.7 μL (0.0337 mmol) of NEt_3 were added to the orange-brown solution at room temperature with an immediate fine cloudiness forming above the reaction mixture and a colour change to deep red. ^{31}P{^{1}H} NMR analysis revealed that after ~15 min of reaction all of the alkylidyne **71b** was consumed and the vinylidene **70b** had been formed, although in very small quantities (35%) along with several other unidentified species based on approximate ^{31}P{^{1}H} NMR spectrum integrations.

PPh_3: 0.0087 g (0.0124 mmol) of **71b** and 0.0112 g (0.0427 mmol) PPh_3 were mixed together in an NMR tube in the solid state, degassed using a vacuum line, and dissolved in 0.3 mL $CDCl_3$ under N_2. The instant loss in orange-brown colour of the solution was observed to give rise to a dark brown solution along with substantial precipitation of a brown solid. While complete consumption of the alkylidyne within 3 hrs. was confirmed by ^{31}P{^{1}H} NMR analysis, 67% of the sample (not including PPh_3) was represented by the vinylidene **70b**, the rest consisting of unidentified species based on approximate ^{31}P{^{1}H} NMR spectrum integrations.

Low-Temperature Observation of $[Cp^{*}RuCl(\equiv C-CH_2(Ph))(PPh_3)][BF_4]$, 71c.

0.0324 g (0.0509 mmol) $Cp^{*}RuCl(=C=CHPh)(PPh_3)$[1] **70c** were dissolved in 0.4 mL CD_2Cl_2 in a 5 mm NMR tube fitted with a rubber septum and attached to a N_2 line. The deep red solution was cooled to −78 °C followed by the addition of 7.4 μL of a 54 wt% solution of HBF_4 in Et_2O (0.0537 mmol) via syringe. An instant colour change from deep red to orange was observed. The NMR data were acquired immediately at −75 °C. Immediate formation of **71c** was observed by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. ^1H NMR (499.9 MHz, CD_2Cl_2, −75 °C): δ 7.58−6.95 (m, 20 H, Ph), 4.05 (d, 1 H, $^2J_{HH} = 20.5$ Hz, $Ru{\equiv}CCH_aH_bPh$), 3.52 (d, 1 H, $^2J_{HH} = 20.5$ Hz, $Ru{\equiv}CCH_aH_bPh$), 1.60 (d, 15 H, $^4J_{PH} = 1.5$ Hz, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2, −75 °C): δ 340.6 (d, $^2J_{PC} = 16.3$ Hz, $Ru{\equiv}C$), 133.9−126.8 (s, Ph), 110.9 (s, $C_5(CH_3)_5$), 59.7 (s, $Ru{\equiv}CCH_2Ph$), 10.0 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_2Cl_2, −75 °C): δ 38.6 (s, PPh_3).

Synthesis of $[Cp^{*}RuCl(\equiv C-CH_2(^tBu))(PPh_3)][B(Ar^f)_4]$, 72a.

Anion metathesis was carried out through dissolution of 0.229 g (0.325 mmol) **71a** in 8 mL CH_2Cl_2. The addition of 0.386 g (0.436 mmol) $Na[B(Ar^f)_4]$[2] in 4 mL Et_2O to this stirred orange solution via cannula at room temperature was accompanied by the immediate formation of a white precipitate. After ~20 min of stirring, the solvents were removed under reduced pressure and the product was extracted from the resultant orange residue with 3 × 12 mL CH_2Cl_2. Filtration of this extract through Celite and solvent removal from filtrate under reduced pressure yielded the analytically pure product as a dark orange-brown solid. Orange single crystals of **72a** were grown through slow diffusion from CH_2Cl_2 with hexanes at −20 °C. Yield: 0.463 g (96%). Anal. Calcd. for $C_{66}H_{53}BClF_{24}PRu{\bullet}CH_2Cl_2$: C, 51.40; H, 3.55. Found C, 51.21; H, 3.75. The presence of solvent was confirmed spectroscopically. ^1H NMR (499.9 MHz, CD_2Cl_2, 22 °C): δ 7.75−7.45 (m, 27 H, Ph and $C_6H_3(CF_3)_2$), 2.51 (d, 1 H, $^2J_{HH} = 20.3$ Hz, $Ru{\equiv}CCH_aH_b(^tBu)$), 1.76 (d, 1 H, $^2J_{HH}$ = 20.3 Hz, Ru≡CCH_aH_b(^{t}Bu)), 1.61 (d, 15 H, $^4J_{PH}$ = 1.5 Hz, $C_5(CH_3)_5$), 0.99 (s, 9 H, $C(CH_3)_3$). $^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2, 22°C): δ 348.3 (d, $^2J_{PC}$ = 15.7 Hz, Ru≡*C*), 161.9 (q, $^1J_{BC}$ = 49.6 Hz, C_{ipso} of Ar^f), 135.0 (s, C_{ortho} of Ar^f), 134.5-129.5 (s, Ph), 129.0 (m, C_{meta} of Ar^f), 124.8 (q, $^1J_{CF}$ = 271 Hz, *C*F_3 of Ar^f), 117.7 (s, C_{para} of Ar^f), 110.6 (s, $C_5(CH_3)_5$), 67.1 (s, Ru≡C*C*H_2(^{t}Bu)), 36.9 (s, *C*Me$_3$), 30.4 (s, $C(CH_3)_3$), 10.1 (s, $C_5(CH_3)_5$). $^{19}F\{^1H\}$ NMR (470.2 MHz, CD_2Cl_2, 22°C): δ -63.2 (s, CF_3 of Ar^f). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_2Cl_2, 22°C): δ 38.3 (s, *P*Ph$_3$).

Structural Characterisation of 72a through X-ray Crystallography.

Orange crystals of **72a** were grown through slow diffusion from a CH_2Cl_2 solution using hexanes as the diffusing solvent at -20°C. One crystal was mounted on a glass fibre and data were collected using a Bruker 1K X-ray diffractometer at -75°C using Mo(Kα) radiation. Lorentz and polarization corrections were applied and data were also corrected for absorption using redundant data and the SADABS program. Direct methods and Fourier techniques were used to solve the crystal structure with refinement being conducted using full-matrix least-squares calculations and SHELXTL PC V 5.03. All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were treated as riding models and updated after each refinement. All $-CF_3$ groups of the B(Ar^f)$_4$ anion showed rotational disorder on all phenyl rings, and one molecule of CH_2Cl_2 solvent was located and refined within the lattice. The largest difference peak (2.903 e.Å^{-3}) was associated with the Ru atom. Crystal data and structure refinement for the complex [Cp*RuCl(≡C-CH$_2$(^{t}Bu))(PPh$_3$)][B(Ar^f)$_4$]•CH_2Cl_2 are presented in Table 5.

Table 5: Crystal data and structure refinement for $[Cp^{*}RuCl(\equiv C-CH_2(^{t}Bu))(PPh_3)][B(Ar^{f})_4]\bullet CH_2Cl_2$

Empirical formula	$C_{67}H_{55}BCl_3F_{24}PRu$
Formula weight	1565.31
Temperature	198(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 17.730(1) Å α = 90°
	b = 19.077(1) Å β = 94.349(1)°
	c = 20.365(1) Å γ = 90°
Volume	6868.3(7) $Å^3$
Z	4
Density (calculated)	1.514 Mg/m^3
Absorption coefficient	0.474 mm^{-1}
F(000)	3152
Crystal size	0.25 × 0.3 × 0.45 mm^3
Theta range for data collection	1.46 to 27.50°
Index ranges	-23<=h<=22, -24<=k<=24, -26<=l<=26
Reflections collected	47451
Independent reflections	15419 [R(int) = 0.0421]
Completeness to theta = 27.50°	97.8%
Absorption correction	none
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15419 / 0 / 1098
Goodness-of-fit on F^2	1.185
Final R indices [I>2sigma(I)]	R1 = 0.0537, wR2 = 0.1529
R indices (all data)	R1 = 0.0871, wR2 = 0.1690
Largest diff. peak and hole	2.903 and 0.928 $e.Å^{-3}$

Synthesis of $[Cp^{*}RuCl(\equiv C-CH_2(^{n}Bu))(PPh_3)][B(Ar^{f})_4]$, 72b.

A similar anion metathesis process used for preparing upon **71a** was carried out through dissolution of 0.195 g (0.277 mmol) of freshly prepared **71b** in 8 mL CH_2Cl_2.

The addition of 0.3344 g (0.3861 mmol) $Na[B(Ar^f)_4]$ in 4 mL Et_2O via cannula to this stirred orange solution at room temperature was accompanied by the immediate formation of a white precipitate. After ~20 min of stirring, the solvents were removed under reduced pressure and the product was extracted from the resultant orange residue with 3 × 12 mL CH_2Cl_2. Filtration of this extract through Celite and solvent removal from the filtrate under reduced pressure yielded the crude product as a dark orange-brown solid. Unfortunately, the extreme solubility of **72b** confounded all attempts at obtaining sufficiently pure samples for elemental analysis. Yield: 0.407 g (99%). ^{1}H NMR (499.9 MHz, CD_2Cl_2, 22 °C): δ 7.66–7.39 (m, 27 H, Ph and $C_6\mathit{H}_3(CF_3)_2$), 2.35 (m, 1 H, $^2J_{HH}$ = 20.5 Hz, $Ru{\equiv}CC\mathit{H}_aH_b(^n\mathrm{Bu})$), 1.86 (m, 1 H, $^2J_{HH}$ = 20.5 Hz, $Ru{\equiv}CCH_a\mathit{H}_b(^n\mathrm{Bu})$), 1.56 (d, 15 H, $^4J_{PH}$ = 1.9 Hz, $C_5(C\mathit{H}_3)_5$), 1.48–1.09 (m, 6 H, $Ru{\equiv}CCH_2(^n\mathit{Bu})$), 0.77 (t, 3 H, $^3J_{HH}$ = 7 Hz, $Ru{\equiv}CCH_2(^n\mathit{Bu})$). $^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2, 22 °C): δ 347.0 (d, $^2J_{PC}$ = 17.1 Hz, $Ru{\equiv}\mathit{C}$), 162.0 (q, $^1J_{BC}$ = 49.6 Hz, C_{ipso} of Ar^f), 135.0 (s, C_{ortho} of Ar^f), 135.8–128.1 (s, Ph), 129.1 (m, C_{meta} of Ar^f), 124.8 (q, $^1J_{CF}$ = 271 Hz, $\mathit{C}F_3$ of Ar^f), 117.7 (s, C_{para} of Ar^f), 110.7 (s, $\mathit{C}_5(CH_3)_5$), 66.1 (s, $Ru{\equiv}C\mathit{C}H_2(^n\mathrm{Bu})$), 31.6 (s, ^{n}Bu), 24.3 (s, ^{n}Bu), 22.1 (s, ^{n}Bu), 13.5 (s, ^{n}Bu), 10.1 (s, $C_5(\mathit{C}H_3)_5$). $^{19}F\{^1H\}$ NMR (470.2 MHz, CD_2Cl_2, 22 °C): δ −63.2 (s, $C\mathit{F}_3$ of Ar^f). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_2Cl_2, 22 °C): δ 38.6 (s, $\mathit{P}Ph_3$).

Synthesis of $[Cp^*Ru(OTf)(=C=CHPh)(PPh_3)]$, 73c.

In a 10 mL Schlenk tube, 0.0460 g (0.0723 mmol) of **70c** were dissolved in 0.5 mL CH_2Cl_2 and treated with 25 μL (0.221 mmol, 3 equivalents) of MeOTf via syringe. An almost immediate colour change from deep red to dark brown with formation of some brown solid was observed. The reaction mixture was stirred at room temperature for 30 min., at which point the volatiles were removed under reduced pressure. The resultant brown solid was then washed with hexanes (4 × 5 mL) and allowed to dry *in vacuo*. Yield: 0.360 g (66%). Anal. Calcd. for $C_{37}H_{36}F_3O_3PRuS{\bullet}2CH_2Cl_2$: C, 50.93; H, 4.39. Found: C, 51.67; H, 4.64. The presence of solvent was confirmed spectroscopically. ^{1}H NMR (499.9 MHz, CD_2Cl_2, 22 °C): δ 7.39–6.89 (m, 20 H, Ph), 4.54 (s, 1 H, $Ru{=}C{=}C\mathit{H}$), 1.39 (d, 15 H, $^4J_{PH} = 2.0$ Hz, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2, 22 °C): δ 344.3 (d, $^2J_{PC} = 22.1$ Hz, Ru=*C*), 134.2-125.2 (s, Ph), 118.9 (q, $^1J_{CF} = 318$ Hz, CF_3SO_3), 115.2 (s, $C_5(CH_3)_5$), 103.4 (s, Ru=C=*C*HPh), 9.88 (s, $C_5(CH_3)_5$). $^{19}F\{^1H\}$ NMR (470.2 MHz, CD_2Cl_2, 22 °C): δ −79.1 (s, CF_3SO_3). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_2Cl_2, 22 °C): δ 47.5 (s, *P*Ph_3).

$^{31}P\{^1H\}$ and ^1H NMR Monitoring of Reaction of 70c with MeOTf

In an NMR tube, 0.0461 g (0.0725 mmol) of $Cp^*RuCl(=C=CHPh)(PPh_3)$ were dissolved in 0.4 mL CD_2Cl_2 under N_2. The addition of 25 μL of MeOTf (0.221 mmol, 3 equivalents) via syringe to this deep red solution at room temperature resulted in an immediate colour change to dark brown with formation of some brown solid. The reaction progress was monitored both by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The complete consumption of the parent vinylidene after 30 min with concomitant quantitative formation of **73c** was indicated by $^{31}P\{^1H\}$ NMR data. Equimolar MeCl was also present in the reaction mixture, as revealed through integration of the obtained ^1H NMR spectra.

Low-Temperature Observation of $[TpRuCl(\equiv C-CH_2(^tBu))(PPh_3)][BF_4]$, 75a.

0.0333 g (0.04798 mmol) of $[TpRuCl(=C=CH(^tBu))(PPh_3)]^4$ **74a** were degassed in an NMR tube and dissolved in 0.4 mL CD_2Cl_2 under N_2. The deep red solution thus formed was then cooled to −78 °C with subsequent addition of 9 μL of a 54 wt% solution of HBF_4 in Et_2O (0.06531 mmol) via syringe. Rapid transfer of the sample tube from the cold bath to a precooled (−70 °C) NMR probe and immediate acquisition of data was then carried out. Quantitative conversion of **74a** into the desired product **75a** was found to be instantaneous. Product decomposition begins at −20 °C with complete decomposition into unidentified species after ~30 hrs. ^1H NMR (499.9 MHz, CD_2Cl_2, −70 °C): δ 7.97 (d, 1 H, $^3J_{HH} = 1.5$ Hz, Tp), 7.84 (s, 2 H, Tp), 7.76 (s, 1 H, Tp), 7.29 (s, 1H, Tp), 7.6-7.2 (m, 15 H, Ph), 6.35 (s, 1 H, Tp), 6.20 (d, 1 H, ${}^3J_{HH}$ = 1.5 Hz, Tp), 6.02 (t, 1 H, ${}^3J_{HH}$ = 2 Hz, Tp), 5.97 (t,1 H, ${}^3J_{HH}$ = 1.5 Hz, Tp), 3.08 (d, 1 H, ${}^2J_{HH}$ = 20.5 Hz, Ru≡CCH_aH$_b$(^{t}Bu)), 2.94 (d, 1 H, ${}^2J_{HH}$ = 20 Hz, Ru≡CCH$_a$$H_b$(^{t}Bu)), 1.00 (s, 9 H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2, −70 °C): δ 355.2 (d, ${}^2J_{PC}$ = 16.5 Hz, Ru≡*C*), 146.9 (s, Tp), 143.7-132.9 (m, Ph), 138.5 (s, Tp), 138.1 (s, Tp), 137.4 (d, ${}^3J_{PC}$ = 2.9 Hz, Tp), 126.3 (s, Tp), 125.9 (s, Tp), 108.6 (s, Tp), 107.6 (d, ${}^4J_{PC}$ = 1.9 Hz, Tp), 107.0 (s, Tp), 70.8 (s, Ru≡C*C*H$_2$(^{t}Bu)), 35.4 (s, *C*Me$_3$), 31.1 (s, C(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (202.3 MHz, CD_2Cl_2, −70 °C): δ 23.9 (s, *P*Ph$_3$).

Low-Temperature Observation of [TpRuCl(≡C−CH$_2$(^{n}Bu))(PPh$_3$)][BF$_4$], 75b.

0.0428 g (0.06167 mmol) of degassed [TpRuCl(=C=CH(^{n}Bu))(PPh$_3$)]^4 **74b** were dissolved in 0.35 mL CD_2Cl_2 in an NMR tube under N_2. The cooling of the deep red reaction mixture to −78 °C was followed by addition of 12 μL of a 54 wt% solution of HBF_4 in Et_2O (0.0648 mmol) via syringe. An instant colour change from deep red to orange-brown was observed. The NMR data were acquired immediately at −75 °C. This data indicated the instantaneous quantitative conversion of **74b** into the desired product **75b**. Product decomposition begins at −20 °C at a rate much faster than that observed with **75a** (complete decomposition within hours). ^{1}H NMR (499.9 MHz, CD_2Cl_2, −70 °C): δ 7.89 (d, 1 H, ${}^3J_{HH}$ = 1.5 Hz, Tp), 7.84 (d, 1 H, ${}^3J_{HH}$ = 2 Hz, Tp), 7.82 (d, 1 H, ${}^3J_{HH}$ = 2.5 Hz, Tp), 7.77 (s, 1H, Tp), 7.62-7.28 (m, 15 H, Ph), 7.09 (s, 1 H, Tp), 6.36 (s, 1 H, Tp), 6.21 (d, 1 H, ${}^3J_{HH}$ = 2 Hz, Tp), 5.99 (m, 2 H, ${}^3J_{HH}$ = 2 Hz, Tp), 3.12-2.96 (m, 2 H, Ru≡CCH_2(^{n}Bu)), 1.92 (br m, 2 H, Ru≡CCH$_2$(*^{n}Bu*)), 1.55 (br m, 2 H, Ru≡CCH$_2$(*^{n}Bu*)), 1.10 (br m, 2 H, Ru≡CCH$_2$(*^{n}Bu*)), 0.73 (t, 3 H, ${}^2J_{HH}$ = 7 Hz, Ru≡CCH$_2$(*^{n}Bu*)). ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2, −70 °C): δ 351.2 (d, ${}^2J_{PC}$ = 17.5 Hz, Ru≡*C*), 146.8 (s, Tp), 143.5-129.3 (m, Ph), 138.2 (s, Tp), 138.1 (s, Tp), 137.2 (s, Tp), 126.6 (s, Tp), 126.2 (s, Tp), 108.3 (s, Tp), 107.7 (d, ${}^4J_{PC}$ = 3 Hz, Tp), 106.9 (s, Tp), 58.1 (s, Ru≡C*C*H$_2$(^{n}Bu)), 32.0 (s, Ru≡CCH$_2$(*^{n}Bu*)), 23.2 (s, Ru≡CCH$_2$(*^{n}Bu*)), 22.5 (s, Ru≡CCH$_2$(*^{n}Bu*)), 14.2 (s, Ru≡CCH$_2$(*^{n}Bu*)). ^{31}P{^{1}H} NMR (202.3 MHz, CD_2Cl_2, −70 °C): δ 26.4 (s, *P*Ph$_3$).

Low-Temperature Observation of $[TpRuCl(\equiv C{-}CH_2(Ph))(PPh_3)][BF_4]$, 75c.

0.0239 g (0.0335 mmol) of $[TpRuCl(=C=CH(Ph))(PPh_3)]$[5] **74c** were degassed and dissolved in 0.4 mL CD_2Cl_2 in an NMR tube under N_2. The resulting deep red solution was then cooled to −78 °C and treated with 5 μL of a 54 wt% solution of HBF_4 in Et_2O (0.0363 mmol) via syringe with a concurrent colour change from deep red to orange-brown. The cooled sample tube was then transferred to a precooled (−70 °C) NMR probe and data were acquired immediately. The instantaneous quantitative conversion of **74c** into the desired product **75c** was confirmed through scrutiny of this data. Slow decomposition of **75c** begins immediately (at −70 °C) and was observed to be completed after ~2 hrs. at room temperature. ^1H NMR (499.9 MHz, CD_2Cl_2, −70 °C): δ 7.81 (d, 1 H, $^3J_{HH} = 2$ Hz, Tp), 7.77 (s, 1 H, $^3J_{HH} = 2.5$ Hz, Tp), 7.60-7.25 (m, 20 H, Ph), 7.23 (s, 1 H, Tp), 7.21 (s, 1H, Tp), 6.32 (s, 1 H, $^3J_{HH} = 2$ Hz, Tp), 6.20 (d, 1 H, $^3J_{HH} = 2.5$ Hz, Tp), 5.97 (t, 1 H, $^3J_{HH} = 2.5$ Hz, Tp), 5.95 (t, 1 H, $^3J_{HH} = 2.5$ Hz, Tp), 5.93 (m, 1 H, $^3J_{HH} = 1$ Hz, Tp), 4.66 (dd, 1 H, $^4J_{PH} = 2$ Hz, $^2J_{HH} = 20$ Hz, $Ru{\equiv}CC\mathit{H}_aH_b(Ph)$), 3.83 (dd, 1 H, $^4J_{PH} = 2$ Hz, $^2J_{HH} = 20.5$ Hz, $Ru{\equiv}CCH_a\mathit{H}_b(Ph)$). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, −70 °C): δ 341.4 (d, $^2J_{PC} = 17.8$ Hz, $Ru{\equiv}\mathit{C}$), 147.1 (s, Tp), 143.4 (s, Tp), 138.0-129.5 (m, $P\mathit{Ph}_3$), 137.4 (d, $^3J_{PC} = 2.9$ Hz, Tp), 131.5 (s, $Ru{\equiv}CCH_2(\mathit{Ph})$), 130.2 (s, $Ru{\equiv}CCH_2(\mathit{Ph})$), 128.6-128.1 (m, $Ru{\equiv}CCH_2(\mathit{Ph})$), 126.5 (s, Tp), 126.1 (s, Tp), 122.9 (s, Tp), 108.3 (s, Tp), 106.8 (d, $^4J_{PC} = 2.9$ Hz, Tp), 63.7 (s, $Ru{\equiv}C\mathit{C}H_2(Ph)$). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_2Cl_2, −70 °C): δ 26.6 (s, $\mathit{P}Ph_3$).

Ambient-Temperature Observation of $[TpRu(OTf)(=C=CH(^tBu))(PPh_3)]$, 76a.

It was determined through experiment that the highest relative quantity of **76a** (~50% based on $^{31}P\{^1H\}$ NMR spectrum integrations) was produced after 15 min of reaction between **74a** and 3 equivalents of MeOTf at room temperature, after which point decomposition of **76a** into several unidentified products occurred. Thus, a sample was prepared in an NMR tube using 0.0360 g (0.05187 mmol) of **74a** and dissolving the degassed solid in 0.5 mL CD_2Cl_2 under N_2. Treatment of the resultant deep red solution with 18 μL of MeOTf (0.159 mmol, 3 equivalents) at −40 °C was followed by tumbling of the reaction at room temperature for 15 min. An instant colour change from deep red to orange-brown was observed. Recooling of the reaction mixture to −40 °C (to freeze the progress of the reaction) was then rapidly effected, as was the insertion of the sample tube into a precooled (−31 °C) NMR probe. Integration of $^{31}P\{^1H\}$ NMR spectra revealed the nearly equivalent presence of both the parent vinylidene **74a** (~40%, δ 40.4 ppm) and the observed product **76a** (~49%, δ 37.7 ppm) as almost exclusive constituents of the reaction mixture. This substantial excess of **76a** made possible the assignment of peaks in the ^1H and $^{13}C\{^1H\}$ NMR spectral data. ^1H NMR (499.9 MHz, CD_2Cl_2, −31 °C): δ 7.88 (d, 1 H, $^3J_{HH} = 2.3$ Hz, Tp), 7.78 (d, 1 H, $^3J_{HH} = 2.3$ Hz, Tp), 7.75 (d, 1 H, $^3J_{HH} = 2.3$ Hz, Tp), 7.64 (d, 1 H, $^3J_{HH} = 2.3$ Hz, Tp), 7.45-7.26 (m, 15 H, Ph), 6.74 (d, 1 H, $^3J_{HH} = 2.3$ Hz, Tp), 6.66 (s, 1 H, Tp), 6.64 (d, 1 H, $^3J_{HH} = 2.3$ Hz, Tp), 6.18 (m, 1 H, $^3J_{HH} = 2.3$ Hz, Tp), 6.03 (m, 1 H, $^3J_{HH} = 2.3$ Hz, Tp), 5.74 (m, 1 H, $^3J_{HH} = 2.3$ Hz, Tp), 4.27 (d, 1 H, $^4J_{PH} = 3$ Hz, $Ru{=}C{=}C\mathit{H}(^tBu)$), 0.99 (s, 9 H, $C(C\mathit{H}_3)_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, −31 °C): δ 373.1 (d, $^2J_{PC} = 16.3$ Hz, $Ru{=}\mathit{C}$), 146.9 (s, Tp), 146.6 (s, Tp), 143.0 (s, Tp), 137.5 (s, Tp), 136.6 (s, Tp), 136.5 (s, Tp), 136.6-128.3 (m, Ph), 118.8 (q, $^1J_{CF} = 319.3$ Hz, $\mathit{C}F_3SO_3$), 107.0 (s, Tp), 106.6 (s, Tp), 106.1 (s, Tp), 105.7 (s, Tp), 39.1 (s, $\mathit{C}Me_3$), 26.8 (s, $C(\mathit{C}H_3)_3$). $^{19}F\{^1H\}$ NMR (470.2 MHz, CD_2Cl_2, −31 °C): δ −79.5 (s, $C\mathit{F}_3SO_3$). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_2Cl_2, −31 °C): δ 37.7 (s, $\mathit{P}Ph_3$).

Ambient-Temperature Observation of $[TpRu(OTf)(=C=CH(^nBu))(PPh_3)]$, 76b.

The reaction of **74b** with 3 equivalents of MeOTf for 15 min at room temperature gave rise to a mixture of species, 56% of which is represented by the observed product **76b**, appearing at δ 39.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum. So, 0.030 g (0.04323 mmol) of **74b** were dissolved in 0.35 mL CD_2Cl_2 in an NMR tube under N_2. To this deep red solution were then added 15 μL MeOTf (0.133 mmol) and an instant colour change to orange-brown was observed. NMR data was acquired after 15 min of reaction. The majority presence of product **76b** therefore facilitates the confident assignment of both ^{1}H and ^{13}C{^{1}H} NMR data. ^{1}H NMR (499.9 MHz, CD_2Cl_2, 22 °C): δ 8.23 (s, 1 H, Tp), 7.89 (d, 1 H, $^3J_{HH}$ = 2 Hz, Tp), 7.65 (d, 1 H, $^3J_{HH}$ = 2 Hz, Tp), 7.61 (s, 1H, Tp), 7.52-7.00 (m, 15 H, Ph), 6.79 (d, 1 H, $^3J_{HH}$ = 2 Hz, Tp), 6.35 (d, 1 H, $^3J_{HH}$ = 1.5 Hz, Tp), 6.08 (m, 1 H, $^3J_{HH}$ = 2 Hz, Tp), 5.72 (m, 1 H, $^3J_{HH}$ = 2 Hz, Tp), 4.35 (td, 1 H, $^4J_{PH}$ =3 Hz, $^3J_{HH}$ = 8.4 Hz, Ru=CC*H*(^{n}Bu)), 2.55 (br m, 2 H, Ru=CCH(^{n}*Bu*)), 1.35 (br m, 2 H, Ru=CCH(^{n}*Bu*)), 1.26 (br m, 2 H, Ru=CCH(^{n}*Bu*)), 0.80 (t, 3 H, $^2J_{HH}$ = 7 Hz, Ru=CCH(^{n}*Bu*)). ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2, 0 °C): δ 369.8 (d, $^2J_{PC}$ = 16.3 Hz, Ru=*C*), 146.9 (s, Tp), 145.4 (s, Tp), 143.6 (s, Tp), 137.4 (s, Tp), 136.7 (s, Tp), 136.4 (s, Tp), 135.3 (d, $^4J_{PC}$ = 2.9 Hz, Tp), 134.2-128.4 (m, Ph), 118.8 (q, $^1J_{CF}$ = 319.3 Hz, *C*F$_3$SO$_3$), 109.0 (s, Ru=C=*C*H(^{n}Bu)), 106.6 (s, Tp), 106.2 (s, Tp), 105.6 (d, $^4J_{PC}$ = 1.9 Hz, Tp), 34.0 (s, Ru=C=CH(^{n}*Bu*)), 22.3 (s, Ru=C=CH(^{n}*Bu*)), 18.3 (s, Ru=C=CH(^{n}*Bu*)), 13.7 (s, Ru=C=CH(^{n}*Bu*)). ^{19}F{^{1}H} NMR (470.2 MHz, CD_2Cl_2, 0 °C): δ -79.1 (s, C*F*$_3$SO$_3$). ^{31}P{^{1}H} NMR (202.3 MHz, CD_2Cl_2, 22 °C): δ 39.0 (s, *P*Ph$_3$).

Ambient-Temperature Observation of [TpRu(OTf)(=C=CH(Ph))(PPh$_3$)], 76c.

The greatest quantity of the observed product **76c** (~89% based on ^{31}P{^{1}H} NMR spectrum integrations) is present in a room temperature reaction mixture consisting of **74c** and 3 equivalents of MeOTf after 90 min of reaction. 0.0323 g (0.0452 mmol) of degassed **74c** were dissolved in 0.35 mL CD_2Cl_2 in an NMR tube under N_2. This deep red solution was then treated with 16 μL MeOTf (0.141 mmol) with a colour change to orange-brown occurring instantly. NMR data were then acquired after 90 min of reaction at room temperature, indicating a nearly quantitative conversion of **74c** to **76c**. ^{1}H NMR (499.9 MHz, CD_2Cl_2, 22 °C): δ 8.38 (d, 1 H, $^3J_{HH}$ = 2.3 Hz, Tp), 7.94 (d, 1 H, $^3J_{HH}$ = 2.3 Hz, Tp), 7.71 (d, 1 H, $^3J_{HH}$ = 2.3 Hz, Tp), 7.66 (m, 1 H, $^3J_{HH}$ = 1.5 Hz, Tp), 7.45-7.03 (m, 20 H, Ph), 6.90 (d, 1 H, $^3J_{HH}$ = 1.5 Hz, Tp), 6.88 (d, 1 H, $^3J_{HH}$ = 1 Hz, Tp), 6.77 (d, 1 H,

$^3J_{HH}$ = 1.5 Hz, Tp), 6.45 (d, 1 H, $^3J_{HH}$ = 2.3 Hz, Tp), 6.18 (t, 1 H, $^3J_{HH}$ = 2.3 Hz, Tp), 6.14 (t, 1 H, $^3J_{HH}$ = 2.3 Hz, Tp), 5.75 (t, 1 H, $^3J_{HH}$ = 2.3 Hz, Tp), 5.40 (d, 1 H, $^4J_{PH}$ =3.5 Hz, Ru=CC*H*(Ph)). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, 22°C): δ 377.4 (d, $^2J_{PC}$ = 17.3 Hz, Ru=*C*), 147.1 (s, Tp), 145.6 (d, $^3J_{PC}$ = 1.9 Hz, Tp), 143.4 (s, Tp), 137.6 (s, Tp), 136.3 (s, Tp), 135.4 (d, $^4J_{PC}$ = 2.9 Hz, Ru=C=CH(*Ph*)), 134.3-130.3 (m, P*Ph*$_3$), 134.1-133.9 (m, Ru=C=CH(*Ph*)), 131.1-130.2 (m, Ru=C=CH(*Ph*)), 128.8-128.5 (m, Ru=C=CH(*Ph*)), 126.9 (s, Tp), 126.1 (s, Tp), 118.9 (q, $^1J_{CF}$ = 319.3 Hz, *C*F_3SO_3), 113.8 (s, Ru=C=*C*H(Ph)), 106.7 (s, Tp), 106.2 (s, Tp), 105.7 (d, $^4J_{PC}$ = 2.9 Hz, Tp). $^{19}F\{^1H\}$ NMR (470.2 MHz, CD_2Cl_2, 22°C): δ -78.9 (s, C*F*$_3SO_3$). $^{31}P\{^1H\}$ NMR (202.3 MHz, CD_2Cl_2, 22°C): δ 37.4 (s, *P*Ph_3).

Attempted Application of 71a to Alkyne Cross Metathesis of MeC≡CPh

These experiments adhered to the following general protocol. The dissolution of ~60 mg (~0.0852 mmol) of freshly-prepared **71a** in 15 mL of CH_2Cl_2 in a three-necked flask attached to both a N_2 line and a vacuum line was followed by the addition of 20 molar equivalents of MeC≡CPh (210 μL, 1.68 mmol) via syringe with subsequent stirring of the light orange reaction mixture. The mixture was then heated to 40°C. During the reaction, a slow stream of N_2 was passed through the reaction mixture under a slight dynamic vacuum. The solvent volume was replenished periodically by adding CH_2Cl_2 via syringe. After 2 hrs., the mixture was allowed to cool to room temperature at which point the solvent was removed under reduced pressure. The resultant residue was then extracted using Et_2O (2 × 10 mL). The Et_2O was removed form the combined extracts under reduced pressure. Analysis of the resulting residues using ^1H and $^{13}C\{^1H\}$ NMR spectroscopy revealed only the presence of starting materials.

(a) Attempted Application of 71a/CuCl to Alkyne Cross Metathesis of MeC≡CPh

An experimental procedure similar to that described above was used, however to the reaction mixture were added 2 molar equivalents of the co-catalyst CuCl (~0.016 g, 0.162 mmol). Upon work up of the reaction mixture and analysis of the resultant residue using ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, only starting materials were observed.

(b) Attempted Application of 71a/$AgBF_4$ to Alkyne Cross Metathesis of MeC≡CPh

A similar procedure as that described above was used with the inclusion of equimolar $AgBF_4$ (~0.013 g, 0.0668 mmol) in the reaction mixture. A colour change from orange to green was observed after ~30 min. of reaction. Analysis of the crude reaction mixture by $^{31}P\{^{1}H\}$ NMR spectroscopy revealed substantial decomposition of **71a** into many unidentified species (~30% **71a**, based on spectral integrations). Work up of the reaction mixture and analysis of the resultant residue using ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy revealed only the presence of starting materials.

3.1 Experimental References

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4. Results and Discussion

Introduction

An interesting facet of this project is the fact that there are essentially two groups of complexes undergoing the same electrophilic attack reactions: those which contain Cp* as the ancillary ligand and those which include Tp as the ancillary ligand. While these ligands are similar in the sense that they are polydentate and sterically demanding, it should be noted that Cp* is a soft donor ligand capable of π-donation/acceptance while Tp is a harder and strictly σ-donating ligand.[1] Another difference is the fact that while Tp imposes a strict octahedral geometry around the metal atom (also capable of η^3, η^2, and η^1 binding modes),[2] Cp derivatives have a fluxional bonding property, being capable of "ring slippage" which changes the number of metal bonding sites the ligand may occupy.[3] The relative steric parameters of these ligands may also be quantified through consideration of their respective cone angles[4]: 182° for Cp* and 262° for Tp, indicating that Tp-alkylidyne precatalyst complexes should be better equipped in terms of sterically-induced dissociation of a labile ligand prior to catalysis.

These ligands have been compared to one another before in a recent case study conducted by Bergman *et al.* in which the ν(CO) values of various transition metal carbonyl complexes containing either ligand were compared to one another.[5] These values were interpreted as an indication of the relative electron-donating properties of the two ligands since the backdonation of electron density from filled orbitals on the metal atom into the antibonding orbitals on CO serve to weaken the C-O bond and decrease the frequency of vibration in relation to the value of 2143 cm^{-1} for free gaseous CO.[6] Although no clear-cut trend could be observed across the d-block elements, it was apparent that the relative electron-donation of Cp* versus Tp depended largely on the identity of the transition metal, the oxidation state of the transition metal, and the other ligands of the complex. Nevertheless, for the Group 8 metals Ru and Os, it was concluded that the Cp* ligand was generally a stronger electron-donating ligand than Tp.

In planning the exploration of the reactivity of Ru-vinylidenes towards electrophiles throughout this project, it was decided that a well-devised study would have to include a range of functional groups on the vinylidene ligands. To fulfill this requirement, Ph, ^{t}Bu, and ^{n}Bu were selected. The properties of these functional groups are very well-defined and differ from one another in both steric and electronic terms. For instance, a study conducted by Prock and Giering quantitatively explored these properties as they related to the metal-binding behaviour of phosphine ligands that utilize these and many other functional groups.[7]

The parameter most generally used by the research community for consideration of the steric dimensions of phosphines and other bulky ligands is the Tolman cone angle.[8] This measures the angle at the centre of a cone which originates at the metal atom and encompasses the entire phosphine ligand. Knowing this, it is easy to understand the relative steric bulk of the ^{t}Bu, ^{n}Bu, and Ph groups based on the cone angles of their corresponding PR_3 species these being 182°,132°, and 145°, respectively. Clearly, ^{t}Bu is the more sterically demanding of the three, ^{n}Bu the least.

This same study also took into account the electronic properties of the above groups through consideration of the pKa values of the corresponding protonated phosphonium species, being 11.4, 8.43, and 2.73, respectively. These observed parameters make it possible to speculate that while the steric demands of these functional groups increase in the order ^{n}Bu 〈 Ph 〈 ^{t}Bu, the Lewis basicity increases in the order Ph 〈 ^{n}Bu 〈 ^{t}Bu. A more sterically-demanding vinylidene functional group in the construction of an alkylidyne complex through protonation of said vinylidene may protect the acidic proton from abstraction by some species in solution. Furthermore, a more Lewis basic functional group may serve to stabilize the positive charge imposed upon the complex as a result of protonation. If the observed stabilities of resultant alkylidynes from this project adhere to these proposed trends, they would be in contradiction to those of Werner's Ru-alkylidynes, in which the ^{t}Bu-substituted alkylidynes were much more unstable than their Ph-substituted analogs. This is likely due to unfavourable steric interactions (Section 1.4.2.2.3).[9]

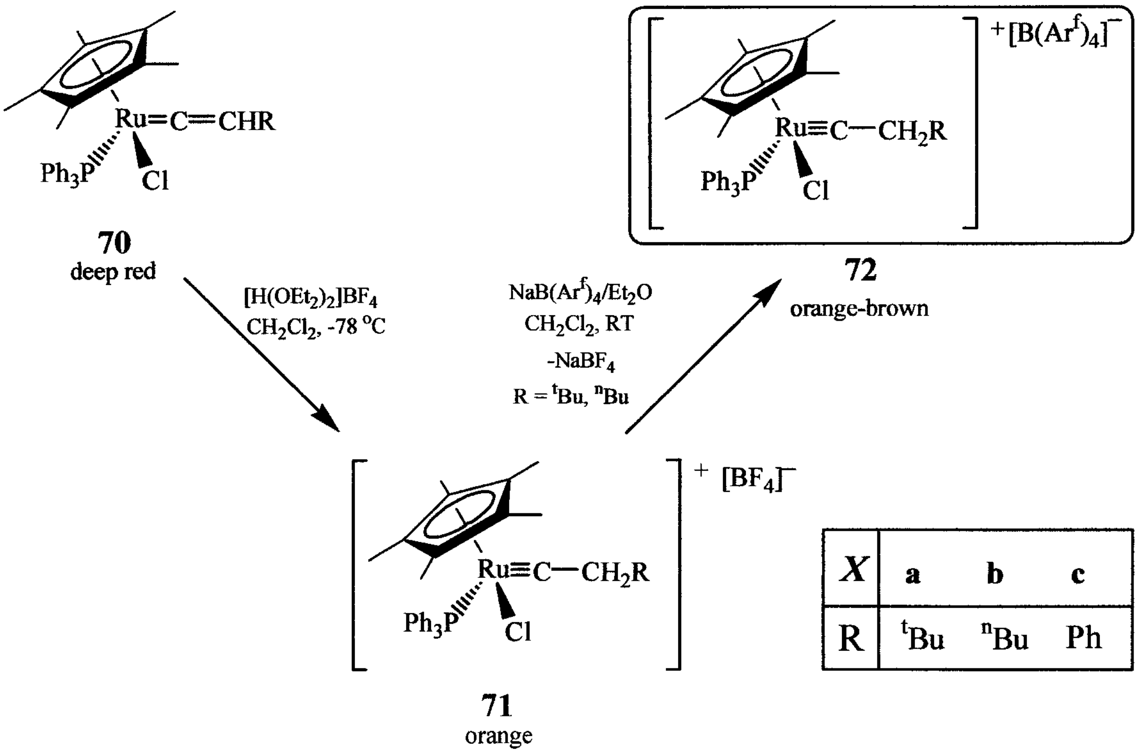
While the relative contributions of the above factors to the overall stability of any resultant alkylidynes is unclear, it will be interesting to speculate on this area once these stabilities have been observed. Having considered the inherent differences of these ligands, it seems most fitting to report upon the results for each ligand system separately. Therefore, the reactions concerning the Cp^*Ru-vinylidenes will be reported first followed by those concerning the TpRu-vinylidenes. A brief section comparing the results of either group will then precede a final section on the attempted application of the stable $[Cp^*RuCl(\equiv C{-}CH_2(^tBu))(PPh_3)][BF_4]$ in the cross metathesis of the internal alkyne $PhC{\equiv}CMe$.

4.1 Protonation Reactions of $Cp^*RuCl(=C=CHR)(PPh_3)$ and $TpRuCl(=C=CHR)(PPh_3)$ Complexes

The reactions pursued during the first phase of the project involved the electrophilic addition reaction of H^+ to a series of Ru-vinylidenes bearing either of the ancillary ligands Cp^* or Tp. These reactions are explained in detail below and outlined in Schemes 49 and 50. The reversibility of this reaction through treatment with a variety of Lewis bases was also studied during this project with the only two alkylidynes which were stable enough for such procedures, namely **71a** (using KO^tBu) and **71b** (using NEt_3 and PPh_3).

4.1.1 *Synthesis and Chemistry of $[Cp^*RuCl(\equiv C{-}CH_2(^tBu))(PPh_3)][BF_4]$, **71a**, and $[Cp^*RuCl(\equiv C{-}CH_2(^tBu))(PPh_3)][B(Ar^f)_4]$, **72a**.*

Upon consideration of the success of the reactions of the first phase of this project, attention is immediately drawn to the protonation reactions of the alkyl-substituted Cp^*Ru-vinylidene starting materials $Cp^*RuCl(=C=CH(^tBu))(PPh_3)$, **70a**,[10] and $Cp^*RuCl(=C=CH(^nBu))(PPh_3)$, **70b** (discussed later in Section 4.1.3). These reactions proceeded with quantitative production of the anticipated products which were then



X	**a**	**b**	**c**
R	^{t}Bu	^{n}Bu	Ph

Scheme 49

observed to possess surprisingly high stabilities. The most successful reaction of this project was the electrophilic addition of H^+ to **70a**. Treatment of a sample of **70a** dissolved in CH_2Cl_2 under N_2 and at −78 °C with a 1.2 molar excess of $HBF_4{\bullet}Et_2O$ was accompanied by an immediate colour change from deep red to orange. Gradual warming to room temperature and removal of the solvent under reduced pressure, followed by Et_2O-rinsing yielded spectroscopically pure $[Cp^*RuCl(\equiv C-CH_2(^tBu))(PPh_3)][BF_4]$, **71a** in good yield.

In an attempt to detect any reactive intermediates which may form during this reaction, a variable temperature NMR experiment was performed by preparing a sample of **70a** in CD_2Cl_2 in an NMR tube and treating this with a 1.2 molar excess of $HBF_4{\bullet}Et_2O$ solution at −78 °C. This reaction mixture was then transferred to a precooled (−75 °C) NMR instrument and data were acquired immediately. Spectral data remained unchanged between −75 °C and 22 °C. The instant quantitative production of **71a** was discovered by analysis of this data, with no detectable intermediates observed. The mechanism of the protonation reaction is unclear (*i.e.*, is initial attack of H^+ at the Ru, C_β, or Cl?), but also indicates the rapidity of this reaction even at extremely low temperatures.

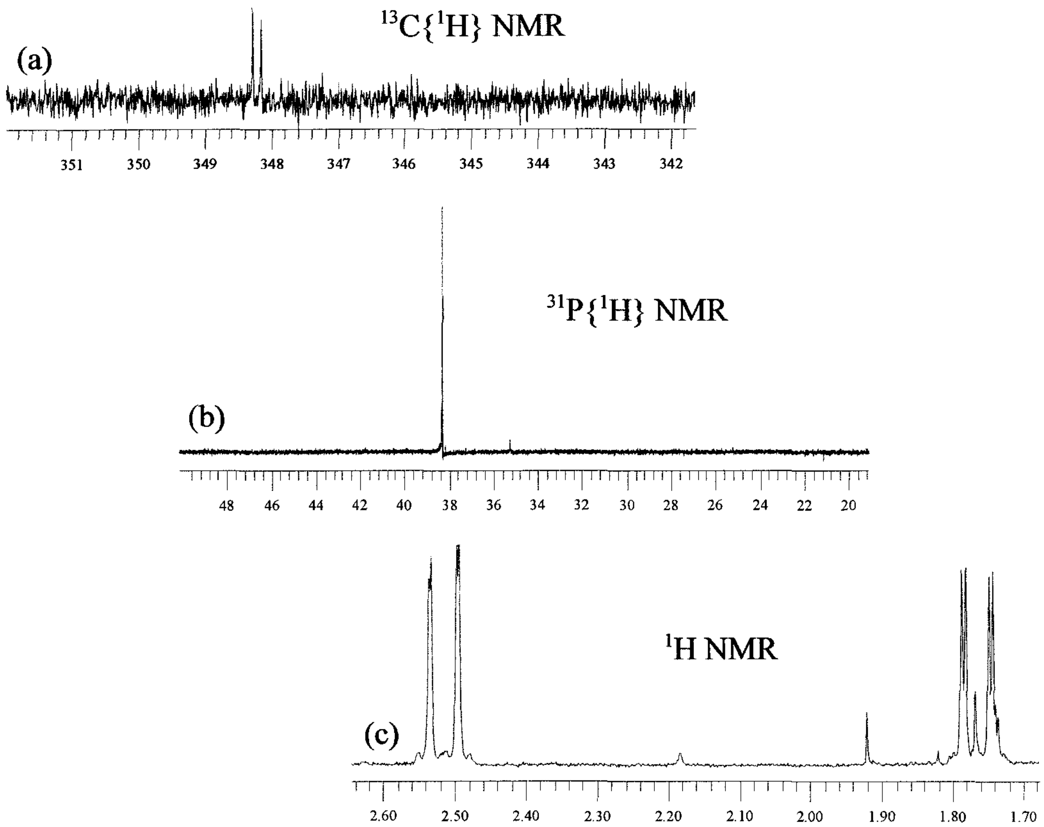
Attempts were made to grow single crystals of **71a** from CH_2Cl_2/Et_2O, CH_2Cl_2/MeOH, and CH_2Cl_2/EtOH, but these endeavours yielded only dark brown oils. It was later discovered that the preparation of a sample of freshly-synthesized **71a** in CD_2Cl_2 in an NMR tube, followed by the addition of excess MeOH resulted in swift (<4 hrs.) decomposition of the complex into unidentified products, which raises the question of whether this complex is vulnerable to either deprotonation or nucleophilic attack at the hands of alcohols. This instability of **71a** toward alcohols was accepted without further investigation.

In order to remedy this, an anion metathesis reaction was undertaken using an Et_2O solution of $Na[B(Ar^f)_4]$ since most other suitable salts (*e.g.*, $NaBPh_4$, $NaPF_6$) require the use of alcohols as reaction solvents. The immediate formation of a white precipitate (likely $NaBF_4$) was observed upon addition of this solution to one of **71a** in CH_2Cl_2. Removal of the solvent under reduced pressure followed by Et_2O-washing yielded the orange-brown analytically pure [Cp*RuCl(≡C−CH$_2$(^{t}Bu))(PPh$_3$)][B(Ar^f)$_4$], **72a**. Further purification of the obtained product through slow diffusion of hexanes into a solution of **72a** in CH$_2$Cl$_2$ at −20°C was carried out successfully to obtain X-ray-quality single crystals.

Characterization of **72a** was carried out using both NMR spectroscopy (Figure 6) and X-ray crystallographic analysis.

The NMR data indicated the formation of the desired complex **72a**. For instance, the far downfield alkylidyne-C$_\alpha$ doublet observed at δ 348.3 ppm in the ^{13}C{^{1}H} NMR spectrum (Figure 6a) was greatly shifted downfield from that of the parent vinylidene **70a** (δ 336.5 ppm in CDCl$_3$).[10] This change in chemical shift corresponds to a decreased shielding of C$_\alpha$, which would be expected to accompany an oxidation of the Ru-atom.[11] Furthermore, the coupling constant of this doublet, which arises from the splitting of C$_\alpha$'s signal by the P atom of the phosphine ligand, is markedly decreased to 15.7 Hz ($^2J_{PC}$ = 23.6 Hz for C$_\alpha$ of **70a**).[10] This decreased interaction between the two atoms is also indicative of oxidation at the Ru-atom since this would result in a decreased backdonation to the phosphine, thereby lengthening the Ru−P bond (see X-ray structure analysis below).[11b] Another feature of the ^{13}C{^{1}H} NMR spectrum is the downfield shifting of the signals corresponding to the Cp* ligand. The signal for the C-atoms of the Cp* ring was found to appear at δ 110.9 ppm, substantially shifted from that of **70a** (δ ~101 ppm).[10] The Me signals were also shifted slightly downfield (δ 10 ppm from δ 9.4 ppm for **70a**).

From the ^{1}H NMR spectrum (Figure 6(c)), the appearance of two doublets of equal integrals at δ 2.51 and 1.76 ppm is very different from the ^{1}H NMR signal for the C$_\beta$-proton of the vinylidene ligand of **70a** (δ ~3.4 ppm). These signals each correspond to the inequivalent methylene protons on C$_\beta$ of **72a**, and, as such, are split by one another ($^2J_{HH}$ = 20.3 Hz). This inequivalence is the result of a chiral Ru-centre and restricted rotation about the C$_\alpha$−C$_\beta$ bond, or about the Ru≡C bond for that matter[12]. When considering the steric bulk of the ligands employed in this complex, it is easy to understand that the crowding of the alkylidyne moiety by both the Cp* and PPh$_3$ ligands serves to lock in place the bulky ^{t}Bu group. Even though chirality around the Ru-



<u>Figure 6:</u> Room Temperature NMR Spectra of 72a in CD_2Cl_2 (selected regions).

atoms of **71a** and **72a** imposes an enantiomeric inequivalence on the methylene hydrogens, VT NMR studies carried out by Herrmann and Baratta et al.[13] have demonstrated the coalescence of inequivalent proton signals in chiral Cp*Ru complexes at high temperatures (~60–65 °C). So strong is the apparent restriction that coalescence of the methylene proton signals is not observed even at 70 °C in C_6D_6, despite the persistence of this complex at this temperature (*i.e.* ~75% based on $^{31}P\{^1H\}$ NMR spectrum integrations). The downfield shifting of the signal corresponding to the Cp*-methyl protons of **72a** (δ 1.61 ppm) relative to **70a** (δ ~1.4 ppm) is also observed, which supports oxidation at the Ru atom.

The X-ray crystal structure of **72a** unequivocally confirms the synthesis of a Ru-alkylidyne (Figure 7). The overall molecular geometry of **72a** is that of a distorted three-legged piano stool and includes a surprisingly short Ru≡C bond length of 1.710(3) Å, which is still longer than that reported for Werner's Ph-substituted alkylidyne (Section 1.4.2.2.3) but much shorter than the Ru=C_α bond lengths in the vinylidene complexes Cp*RuCl(=C=CH(R))(PPh$_3$) (R = Ph, SiMe$_3$) (1.80 to 1.85 Å),[10] and indicative of a Ru≡C bond. The oxidation of the Ru metal is also reinforced by the observation of a longer Ru–P bond (2.3641(9) Å) compared to those of the aforementioned vinylidene complexes, in which these bond lengths fall within the range of 2.305-2.315 Å.[10] The shorter Ru–Cl bond length of 2.3715(9) Å relative to these vinylidenes (2.395-2.408 Å)[10] also supports oxidation. As an indication of the intense steric crowding of this complex, the crystal structure of **72a** also reveals a slightly bent Ru–C_α–C_β angle of 174.1(3)° from the 180° expected for linear *sp*-hybridized C_α. Table 5 (see Experimental Section) contains the crystal data and structure refinement for the complex [Cp*RuCl(≡C–CH$_2$(^{t}Bu))(PPh$_3$)][B(Ar^f)$_4$]•CH$_2$Cl$_2$, and Table 6 catalogues the various pertinent bond lengths and bond angles of this species.

The stability of **72a** towards thermal stress and the open atmosphere is astounding to say the least. It has already been mentioned that this complex has exhibited considerable thermal stability in the solution phase (see above account of NMR analysis). Quite unexpected is the observation that **72a** exhibits little decomposition in airless solution at ambient temperatures over a period of days and virtually no decomposition in the solid form for months under these conditions, in contradiction to the trends seen with Werner's alkylidynes (Section 1.4.2.2.3).[9] **72a** does, however, exhibit moderate air sensitivity, with ~20% decomposition observed after a 1 hr air-exposure of a freshly-prepared sample of **72a**, based on $^{31}P\{^1H\}$ NMR spectrum integrations. After exposure to air over 48 hrs., the final decomposition mixture consists mainly of $[HPPh_3]^+$ ($^{31}P\{^1H\}$ NMR, δ 23.6 ppm, CD_2Cl_2) as determined by comparison to an authentic sample prepared from PPh_3 and HCl(aq) ($^{31}P\{^1H\}$ NMR, δ 22.6 ppm, $CDCl_3$). Nevertheless, common in-air handling procedures of the exhaustively dried solid (*i.e.*, collecting, weighing) seem sufficient.

Table 6: Selected Bond Lengths and Bond Angles for $[Cp^*RuCl(\equiv C-CH_2(^tBu))(PPh_3)][B(Ar^f)_4] \bullet CH_2Cl_2$

Selected Bond Lengths (Å)	Selected Bond Angles (°)
Ru(1)-C(11) = 1.710(3)	C(11)-Ru(1)-P(1) = 90.06(11)
Ru(1)-P(1) = 2.3641(9)	C(11)-Ru(1)-Cl(1) = 101.41(11)
Ru(1)-Cl(1) = 2.3715(9)	P(1)-Ru(1)-Cl(1) = 90.22(3)
Ru(1)-C(1) = 2.392(3)	C(12)-C(11)-Ru(1) = 174.1(3)
Ru(1)-C(2) = 2.391(3)	
Ru(1)-C(3) = 2.255(3)	
Ru(1)-C(4) = 2.232(3)	
Ru(1)-C(5) = 2.240(3)	

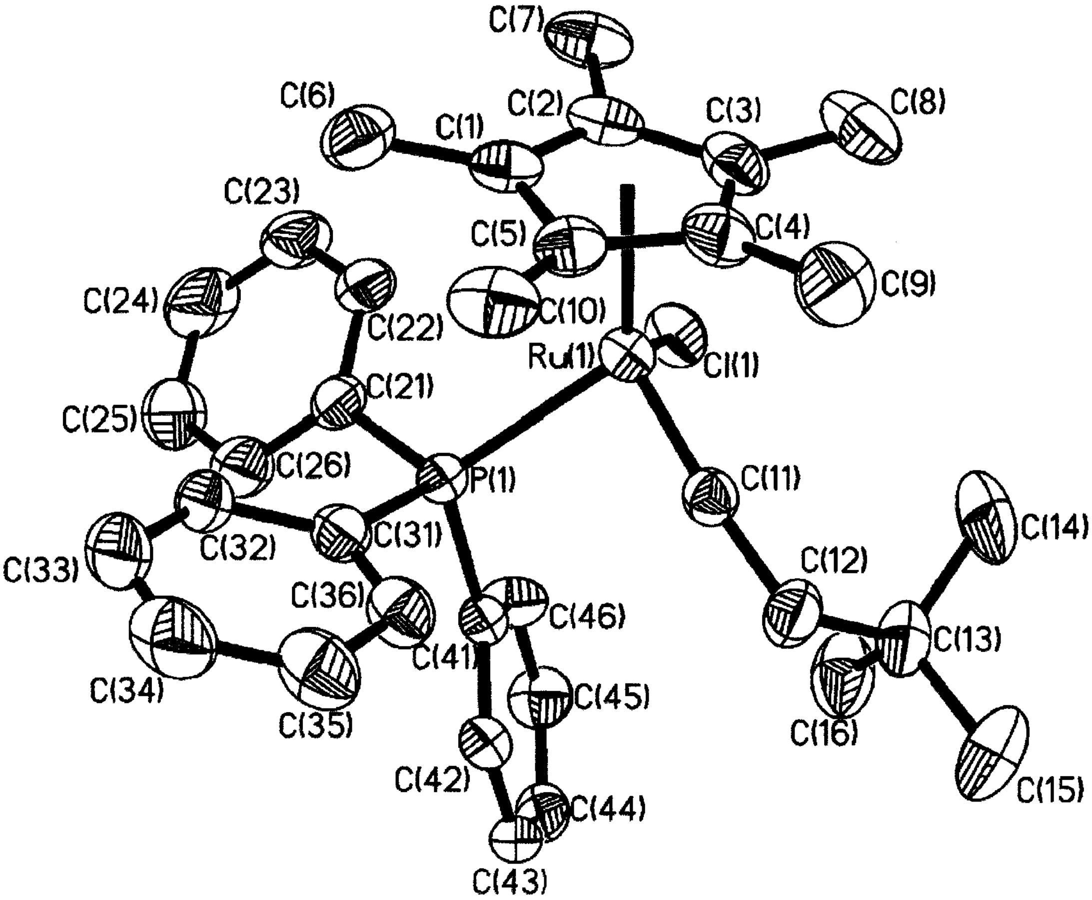


Figure 7: ORTEP Drawing of $[Cp^{*}RuCl(\equiv C-CH_2(^{t}Bu))(PPh_3)][B(Ar^{f})_4]\bullet CH_2Cl_2$

(H atoms, $B(Ar^{f})_4^{-}$ counteranion, and CH_2Cl_2 solvate omitted for clarity)

4.1.2 *Reversibility of the **70a** Protonation Reaction.*

The reversibility of this protonation reaction, as seen with protonated Ru-allenylidenes (Section 1.4.2.7), was investigated through the treatment of **71a** with the strong Lewis base KO^{t}Bu. This was performed via the addition of 0.5 equivalents (*i.e.*, enabling simultaneous observation of alkylidyne and vinylidene species) of KO^{t}Bu (1.0 M in THF) to a concentrated sample of **71a** in CD_2Cl_2 in an NMR tube under N_2, then monitoring the progress of the reaction using $^{31}P\{^1H\}$ NMR spectroscopy. The sample underwent an instant colour change from deep orange-brown to dark red with the appearance of a white solid in the tube (presumably KBF_4). The $^{31}P\{^1H\}$ NMR spectrum revealed the nearly equal presence of both the alkylidyne species **71a** at δ 39.1 ppm and the vinylidene species **70a** at δ 52.4 ppm. $^{13}C\{^1H\}$ NMR data acquired from this reaction mixture clearly displays low-field doublets for both the alkylidyne **71a** and vinylidene species, Cp*RuCl(=C=CH(^{t}Bu))(PPh$_3$), **70a**. It should be noted that the $\delta(C_\alpha)$ values were skewed slightly (**70a**, δ 336.4 ppm; **71a**, δ 351.2 ppm) from their normal positions in neat CD_2Cl_2 (**70a**, δ 336.5 ppm; **71a**, δ 351.0 ppm). The characteristic $^2J_{PC}(C_\alpha)$-values for **70a** and **71a** were also skewed slightly (**70a**, 23.0 Hz; **71a**, 16.3 Hz) compared to the accepted values of 23.6 and 15.7 Hz, respectively. These differences are attributable to the presence of THF in the reaction mixture.

4.1.3 *Synthesis and Chemistry of Cp*RuCl(=C=CH(^{n}Bu))(PPh$_3$), **70b**, [Cp*RuCl(≡C-CH$_2$(^{n}Bu))(PPh$_3$)][BF$_4$], **71b** and [Cp*RuCl(≡C-CH$_2$(^{n}Bu))(PPh$_3$)][B(Ar^f)$_4$], **72b**.*

In order to investigate the synthesis of **72b**, the as yet unreported vinylidene precursor Cp*RuCl(=C=CH(^{n}Bu))(PPh$_3$), **70b**, had to be synthesized first. This was easily accomplished by extending the experimental method given for **70a**[10] using HC≡C^{n}Bu in place of HC≡C^{t}Bu. Thus, [Cp*RuCl(PPh$_3$)$_2$] was heated under reflux with five molar equivalents of HC≡C^{n}Bu in benzene with a colour change from orange to deep clear red after ~1 hr. of reaction being taken as an indication of reaction completion. Removal of the solvent under reduced pressure and recrystallization from CH_2Cl_2/MeOH yielded analytically pure **70b**. The presence of phosphine contamination of [$Cp^*RuCl(PPh_3)_2$] resulted in the partial conversion of **70b** back to [$Cp^*RuCl(PPh_3)_2$] during recrystallization via replacement of the relatively labile vinylidene ligand, a process which has been previously reported with neutral Ru-vinylidenes.[10,14] This was a constant frustration during the study of this complex. Resolution of this difficulty was achieved by rinsing the crude [$Cp^*RuCl(PPh_3)_2$] several times with Et_2O, then recrystallizing this complex from CH_2Cl_2/hexanes to yield the pure, phosphine-free starting material. The use of five molar equivalents of alkyne in the synthesis of **70b** was sufficient to suppress this widespread reaction reversal caused by the one molar equivalent of phosphine produced during this preparation.

When pure samples of **70b** were treated with a 1.2 molar excess of $HBF_4{\bullet}Et_2O$ at −78 °C under N_2, the expected red to orange colour change occurred immediately. A VT NMR study of this reaction was also carried out by treating a cooled (−78 °C) sample of **70b** in CD_2Cl_2 with HBF_4 in an NMR tube with immediate acquisition of NMR data using a precooled (−75 °C) instrument. The data obtained at this temperature revealed that the sole product [$Cp^*RuCl(\equiv C-CH_2(^nBu))(PPh_3)$][$BF_4$], **71b**, is formed instantly and quantitatively with no detectable intermediates observed, attesting to the rapidity of this reaction. This spectral data remained unchanged between −75 °C and 22 °C. In much the same fashion as **72a**, anion metathesis with addition of Na[$B(Ar^f)_4$] in Et_2O resulted in the quantitative production of the $B(Ar^f)_4^-$ salt [$Cp^*RuCl(\equiv C-CH_2(^nBu))(PPh_3)$][$B(Ar^f)_4$], **72b**.

Like **72a**, the characterization of **72b** depends strongly on NMR data (Figure 8). The characteristic doublet at δ 347.0 ppm ($^2J_{PC}$ = 17.1 Hz) in the $^{13}C\{^1H\}$ NMR spectrum (Figure 8(a)) is indicative of an oxidation at the metal, being downfield from that of the vinylidene **70b** (δ 334.7 ppm). The decreased coupling constant of this doublet relative to that of **70b** ($^2J_{PC}$ = 24.4 Hz) is also strongly indicative of this fact.[11] That the signal is similar to that of the fully-characterized **72a** supports the successful protonation of **70b**,

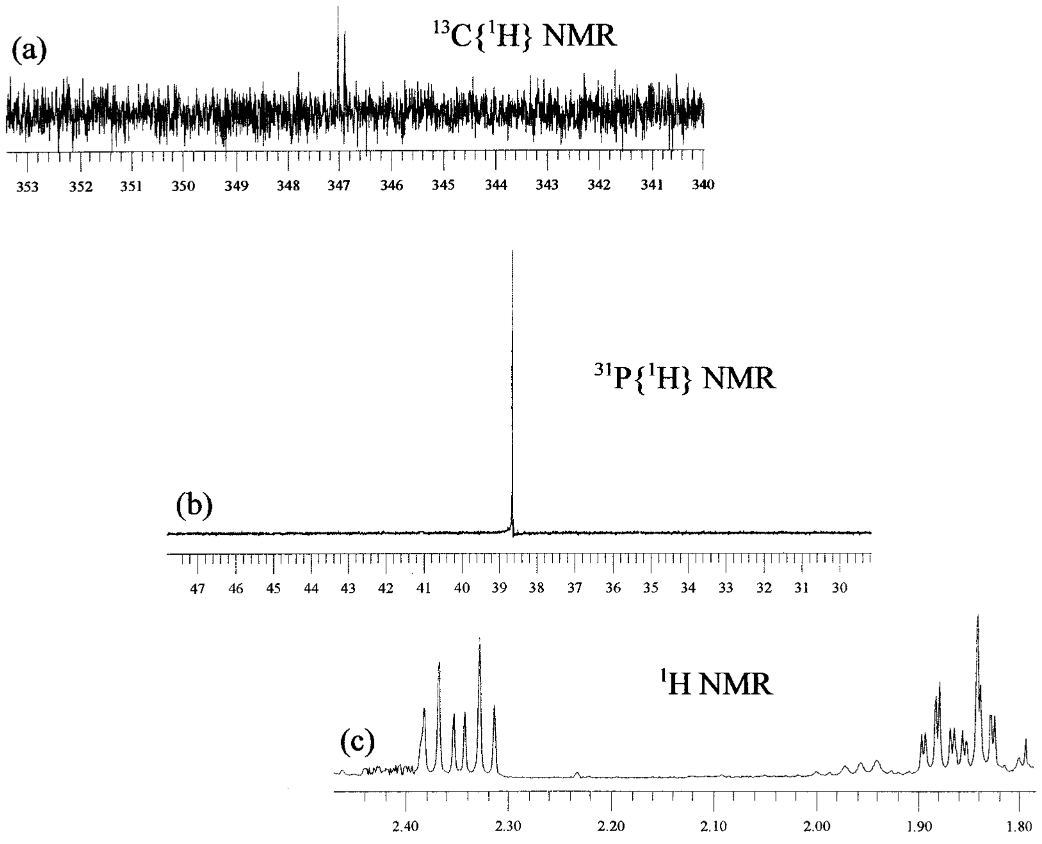


Figure 8: Room Temperature NMR Spectra of 72b in CD_2Cl_2 (selected regions).

as well as implications derived thereof toward Ru-atom oxidation (Section 4.1.1). Also observed in the $^{13}C\{^1H\}$ NMR spectrum is the downfield shifting of the singlets corresponding to the ring and methyl C-atoms of the Cp* ligand, which further supports the formation of **72b**.

From the ^1H NMR spectrum (Figure 8(c)), it was observed that the signal for the vinylidene hydrogen, indicated by a triplet at δ 3.57 ppm ($^3J_{HH}$ = 7.3 Hz), was replaced by a pair of multiplets at δ 2.35 and 1.86 ppm ($^2J_{HH}$ = 20.5 Hz) corresponding to the methylene hydrogens of the alkylidyne ligand. The inequivalence of these hydrogen atoms is the result of the chirality at the Ru atom, as observed with **72a**. This might also indicate steric restriction of rotation about the $C_\alpha - C_\beta$ bond in **72b** even though this complex utilizes the less sterically-demanding ^{n}Bu functional group. An attempt at overcoming this apparent rotational barrier unfortunately failed since the stability of **72b** is such that nearly complete decomposition is observed after several hours in a room temperature CD_2Cl_2 solution, forming mainly $[HPPh_3]^+$. Heating a C_6D_6 solution of **72b** accelerates this process, and complete decomposition occurred (~50 °C) before coalescence of the methylene signals could be observed. As with **72a**, the doublets in the ^1H NMR spectrum at δ 1.45 ppm ($^4J_{PH}$ = 1.5 Hz) for the Cp*-methyl protons of **70b** were also found further downfield at δ 1.56 ppm ($^4J_{PH}$ = 1.9 Hz).

4.1.4 *Reversibility of the **70b** Protonation Reaction.*

The deprotonation of **71b** using a suitable base was also attempted. Treatment of a solution of **71b** in $CDCl_3$ in an NMR tube with either of the Lewis bases NEt_3 and PPh_3 yielded, upon brief reaction (~15 min.), complex product mixtures. For instance, the reaction of **71b** with three molar equivalents of NEt_3 results in the total consumption of the alkylidyne complex with partial formation of the parent vinylidene, $Cp^*RuCl(=C=CH(^nBu))(PPh_3)$, **70b**, as well as several other unidentified compounds, based on $^{31}P\{^1H\}$ NMR analysis. Similar results were observed in the reaction between **71b** and PPh_3, but no occurrence of the vinylidene could be detected.

4.1.5 *Synthesis of [Cp*RuCl(≡C-CH$_2$(Ph))(PPh$_3$)][BF$_4$], 71c.*

Unlike the alkyl-substituted alkylidynes **72a** and **72b**, synthesis of the Ph-substituted analog was not readily achieved. Ironically, the preparation of [Cp*RuCl(=C=CH(Ph))(PPh$_3$)], **70c**,[10] is definitely the simplest to prepare of all Cp*-substituted starting materials used during this project. Even moderate phosphine contamination does not seem to result in significant product decomposition.

Like the other vinylidenes examined as part of this work, synthesis of **70c** required stirring of [Cp*RuCl(PPh$_3$)$_2$] with excess HC≡CPh, followed by recrystallization from CH$_2$Cl$_2$/hexanes. Subsequent treatment of this material with a 1.2 molar excess of HBF$_4$•Et$_2$O at −78 °C produces a colour change from deep red to orange. However, upon warming of the reaction mixture to room temperature and analysis of the products therein, the main constituent is found to be [HPPh$_3$]$^+$ based on the analysis of the ^{31}P{^{1}H} NMR spectrum of the reaction mixture.

Surprisingly, only at low temperatures may the alkylidyne **71c** be observed. This contradicts the stability trend observed with Werner's dichloro(alkylidynes).[9] Nevertheless, treatment of a CD$_2$Cl$_2$ solution of **70c** under N$_2$ with HBF$_4$•Et$_2$O in an NMR tube at −78 °C followed by immediate acquisition of NMR data (Figure 9) using a precooled NMR probe (−75 °C) revealed the quantitative formation of the desired alkylidyne complex [Cp*RuCl(≡C−CH$_2$(Ph))(PPh$_3$)][BF$_4$], **71c**.

The immediate appearance in the low-field region of the ^{13}C{^{1}H} NMR spectrum of a doublet at δ 340.6 ppm (Figure 9(a)) is not so much indicative of an oxidation at the Ru atom since the analogous signal for **70c** appears at δ 340.1 ppm in CD$_2$Cl$_2$. However, the value of the $^2J_{PC}$ coupling constant for **71c** ($^2J_{PC}$ = 16.3 Hz) of the alkylidyne signal is much smaller than that observed for the vinylidene precursor **70c** ($^2J_{PC}$ = 24.4 Hz). This spectrum also reveals the disappearance of the signal corresponding to C_β of the vinylidene ligand at δ 102.4 ppm and the appearance of the methylene C-atom at δ 59.7 ppm, further supporting the success of this synthesis.

Two interesting features of the ^{1}H NMR spectrum (Figure 9(c)) are the pair of doublets corresponding to the the two hydrogen atoms on C_β of the alkylidyne ligand. These signals appear at δ 3.89 and 3.75 ppm (at −75 °C) and diverge upon warming of the NMR instrument (0.46 ppm divergence from −75 °C to +5 °C). The higher-field doublet appears clearly until −15 °C (at δ 3.51 ppm), above which point it becomes completely masked by the residual Et_2O signal from the $HBF_4{\bullet}Et_2O$. The lower-field doublet, on the other hand, persists until the decomposition temperature of +5 °C, making its final appearance at δ 4.10 ppm. While it is unclear why these signals diverge in this manner upon an increase in temperature, the fact that there are two separate doublets of equal integrations and identical coupling constants ($^2J_{HH}$ = 20.5 Hz) is consistent with a chiral Ru-centre and/or a restriction of free rotation about the $C_\alpha - C_\beta$ bond, as is observed with **72a** and **72b**. One possible explanation for this spectral behaviour is that the similarity of the chemical shifts of the signals for the two methylene hydrogen atoms may be causing a second order intensity perturbation of these signals (*i.e.*, the multiplet in Figure 9c epitomizes a second order AB signal pattern).[15] This also explains, at least in part, the observed divergence of these signals as the temperature of the reaction mixture is increased, especially since the appearance of second order AB patterns sometimes exhibits a temperature dependence.

Study of this reaction using VT NMR spectroscopy has revealed that **71c** is unstable even at low temperatures. The sharp increase in the rate of decomposition is observed at around −10 °C with complete decomposition occurring within minutes at +5 °C. This surprising lack of thermal stability precluded further investigation into the reactivity of this complex. The coalescence of the methylene hydrogen signals was not observed before complete decomposition took place.

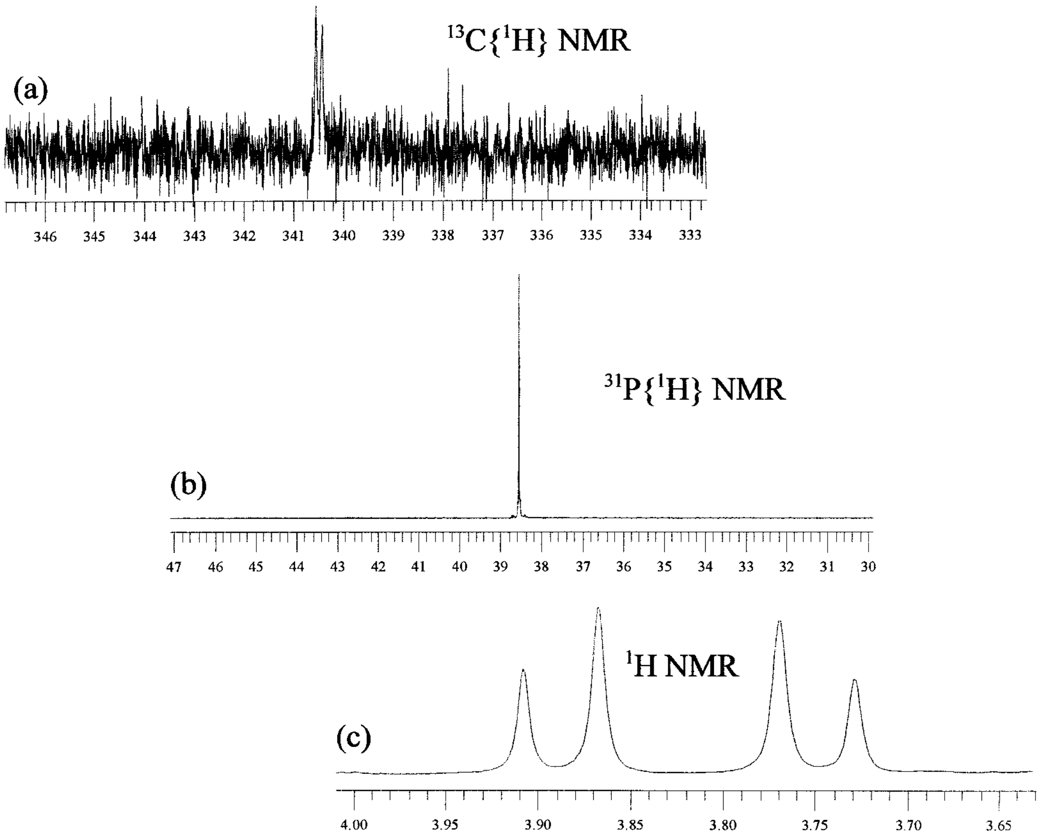
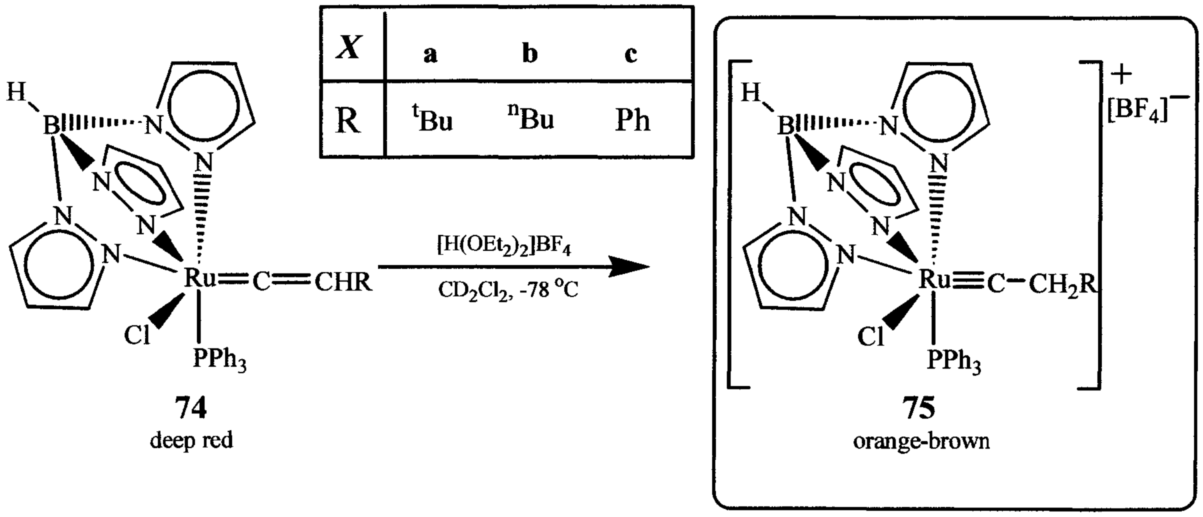


Figure 9: **Low-Temperature (−75°C) NMR Spectra of 71c in CD_2Cl_2 (selected regions).**

4.1.6 *Low-Temperature Observation of $[TpRuCl(\equiv C-CH_2(^tBu))(PPh_3)][BF_4]$*, ***75a***.

The second phase in the investigation of Ru-vinylidene protonation reactions involved the Tp analogues $[TpRuCl(=C=CH(R))(PPh_3)]$ of complexes **70a-c**. The products from these reactions proved to be exceedingly unstable compared to their Cp* counterparts. These studies were initiated using the ^{t}Bu-vinylidene complex $[TpRuCl(=C=CH(^tBu))(PPh_3)]$, **74a**. Unlike the Cp* analogue, the ^{t}Bu-substituted starting material was often prepared in low yield and poor purity, despite the availability of literature preparations.[14c] Several alternative synthetic strategies for this vinylidene were futilely pursued in the course of this project, all of which did not yield any significant results. Nevertheless, the literature preparations were then revisited and the analytically pure starting vinylidene was prepared, albeit with persistent difficulty, thereby facilitating the study of its reactivity toward electrophiles (Scheme 50).[14c]

When a sample of **74a** in an NMR tube under N_2 in CD_2Cl_2 is treated with a 1.2 molar excess of $HBF_4 \bullet Et_2O$ at − 78 °C, a colour change from red to orange-brown was observed immediately. The sample reaction mixture was then transferred to a precooled (− 70 °C) NMR probe and spectral data were acquired immediately (Figure 10). Consideration of the $^{31}P\{^1H\}$ NMR spectrum indicated the immediate quantitative formation of the desired compound **75a** at this temperature, with all of the parent vinylidene having been consumed (Figure 10(b)).



X	**a**	**b**	**c**
R	^{t}Bu	^{n}Bu	Ph

74
deep red

75
orange-brown

Scheme 50

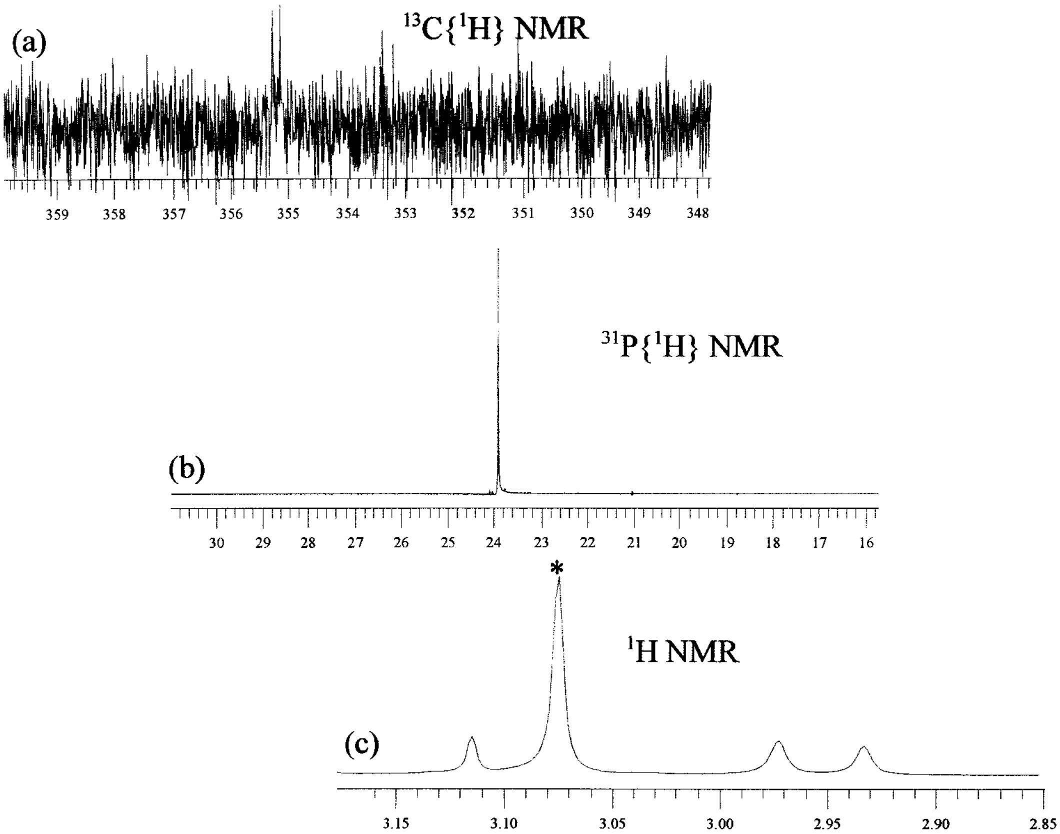


Figure 10: **Low-Temperature (–70 °C) NMR Spectra of 75a in CD_2Cl_2 (selected regions).**

“*” ≡ impurity signal masking product signal

As an indication that the desired alkylidyne had been prepared, there was observed two equal integration doublets in the ^{1}H NMR spectrum (Figure 10(c)) at δ 3.08 ppm ($^2J_{HH}$ = 20.5 Hz) and δ 2.94 ppm ($^2J_{HH}$ = 20 Hz) which correspond to the enantiomerically inequivalent methylene hydrogens of the alkylidyne ligand. The spectrum provided in Figure 10(c) has one of the peaks of the lower-field doublet signal masked by an impurity signal. Further scrutiny of the ^{1}H NMR spectrum revealed that the multitude of signals corresponding to the protons of the Tp ligand of **75a** had shifted downfield relative to those of the parent vinylidene **74a** from δ 8.10-5.73 to δ 7.97-5.97 ppm (see Experimental Section). This is consistent with oxidation at the Ru metal of **75a**. This is not unlike the observed change in chemical shifts for the Cp*-proton signals of **71a-c** which follow oxidation of the Ru atom (Sections 4.1.1, 4.1.3, and 4.1.5). Precedent also exists for this phenomenon in the work of Gunnoe and White et al.[16] in which there is observed a similar change in chemical shift for the Tp-proton signals upon oxidation of the Ru atom of TpRu(CO)(PPh$_3$)(NHPh) by AgOTf.

The success of this reaction is also supported by the appearance of a low-field doublet signal in the ^{13}C{^{1}H} NMR spectrum of **75a** at δ 355.2 ppm ($^2J_{PC}$ = 16.5 Hz) (Figure 10(a)). The decreased coupling constant relative to **74a** (δ 365.1 ppm, $^2J_{PC}$ = 19.2 Hz) is also consistent with the oxidation of the Ru atom as it reveals a decreased interaction between C_α and the P atom of PPh$_3$ upon protonation of **74a**. As with the Tp-proton signals from the ^{1}H NMR spectrum, those signals in the ^{13}C{^{1}H} NMR spectrum which correspond to the Tp-ligand of **75a** are also observed to undergo a general shifting downfield from δ 145.3-105.4 to δ 146.9-107.0 ppm, once again supporting metal oxidation (see Experimental Section).

Unlike the Cp*-analogues **71a** and **72a**, the observed alkylidyne species **75a** does not exhibit significant stability. Specifically, the onset of decomposition in solution is observed at −20 °C and accelerates rapidly upon warming to room temperature as determined by multinuclear VT NMR studies. Almost complete decomposition into unidentified species occurs upon standing of a solution of **75a** at room temperature for 24 hrs. with ~15% alkylidyne species remaining at this point, as indicated by ^{31}P{^{1}H} NMR analysis. It is for this reason that no additional studies on the chemistry or structure of this complex were possible.

4.1.7 *Low-Temperature Observation of [TpRuCl(≡C-CH$_2$(^{n}Bu))(PPh$_3$)][BF$_4$],* ***75b.***

The extension of the protonation reaction to the ^{n}Bu-substituted vinylidene [TpRuCl(=C=CH(^{n}Bu))(PPh$_3$)], **74b**, did not yield readily interpretable results as those observed in the protonation of **74a**. Thus, to a sample of **74b** in an NMR tube under N_2 in CD_2Cl_2 was added 1.2 molar excess of HBF_4•Et_2O at −78 °C. This addition was instantly followed by the familiar colour change from deep red to orange-brown. As quickly as possible, the sample tube was transferred from the cold bath to a precooled (−70 °C) NMR probe with immediate acquisition of NMR data (Figure 11).

The ^{1}H NMR spectrum obtained from this reaction mixture at −70 °C revealed that the multiplet signal at δ 4.05 ppm corresponding to the vinylidene hydrogen of the starting material **74b** had disappeared and was replaced by an elaborate multiplet signal appearing at δ 3.04 ppm, which corresponds to the hydrogens on C_β of the alkylidyne ligand. An overall downfield shift in the signals which correspond to the protons of the Tp-ligand was also observed, from δ 8.22-5.71 to δ 7.89-5.99 ppm which supports oxidation at the Ru atom of **74b.**[16]

A downfield shift of the signals for the Tp-ligand similar to that of **75a** was observed in the ^{13}C{^{1}H} NMR spectrum as well, from δ 145.3-105.4 to δ 146.8-106.9 ppm. The characteristic low-field doublet signal in this spectrum appearing at δ 351.2 ppm ($^2J_{PC}$ = 17.5 Hz) further supports oxidation since the decreased coupling constant relative to **74b** ($^2J_{PC}$ = 19.2 Hz) suggests a weaker interaction between C_α and the P atom of PPh$_3$ upon protonation.

The stability of this new alkylidyne complex is much lower than that of **75a**. While the onset of decomposition occurs at around the same temperature as **75a** (−20 °C), the process is much more rapid with ~35% decomposition occurring after 30 min. of standing at 10 °C, as determined by integration of the ^{31}P{^{1}H} NMR spectrum. This

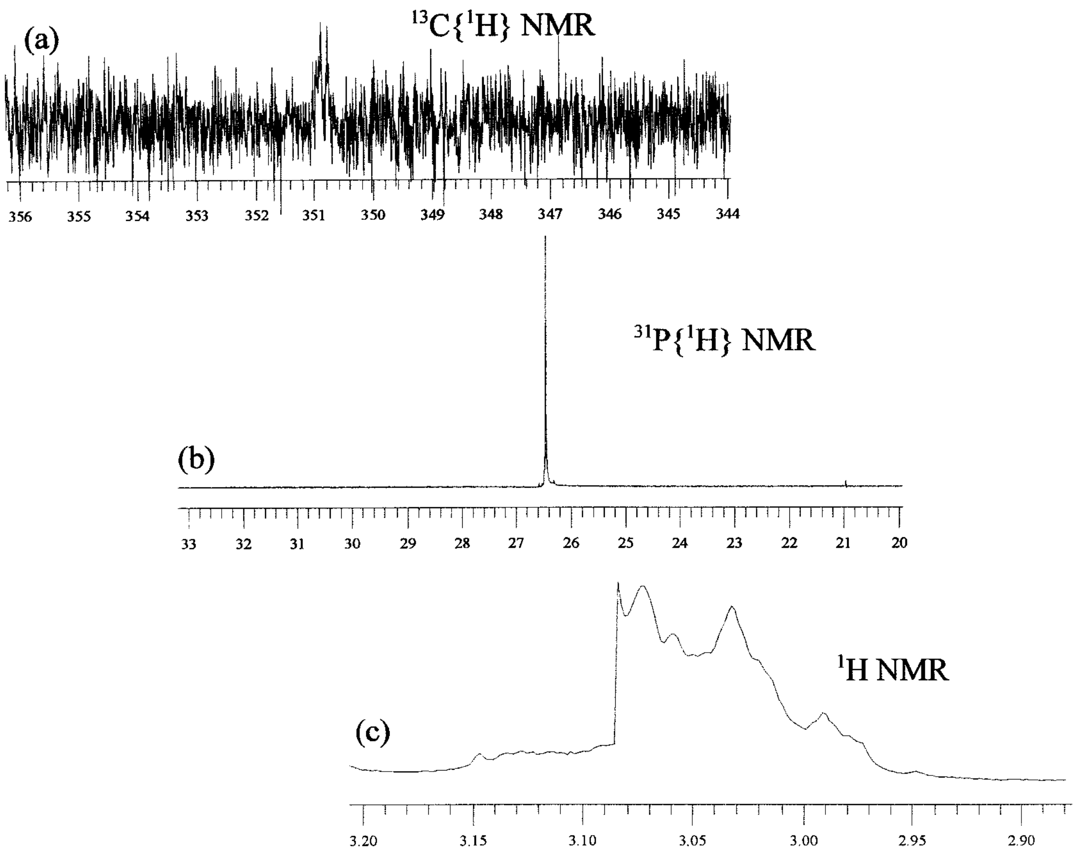


Figure 11: **Low-Temperature (−70 °C) NMR Spectra of 75b in CD_2Cl_2 (selected regions).**

instability precluded further studies of **75b**.

4.1.8 *Low-Temperature Observation of [TpRuCl(≡C-CH$_2$(Ph))(PPh$_3$)][BF$_4$], 75c.*

The least stable Ru-alkylidyne formed during the course of this project involved using the Ph-substituted starting material [TpRuCl(=C=CH(Ph))(PPh$_3$)], **74c**. A sample of **74c** in an NMR tube under N_2 was dissolved in CD_2Cl_2 and cooled to -78 °C. Once cool, a 1.2 molar excess of HBF_4•Et_2O was added via syringe and the acquisition of NMR data (Figure 12) was carried out once the sample tube was transferred to a precooled (-70 °C) NMR probe.

The disappearance of the doublet signal of the vinylidene hydrogen at δ 4.92 ppm ($^4J_{PH}$ =3.8 Hz) in the ^{1}H NMR spectrum was accompanied by the appearance of a pair of doublets at δ 4.66 and 3.83 ppm (Figure 12c) which correspond to the enantiomerically inequivalent methylene hydrogens of the alkylidyne species. A general downfield shifting of the signals representing the hydrogens of the Tp-ligand is also observed from δ 7.88-5.75 to δ 7.81-5.93 ppm. This further supports the oxidation of the Ru atom during the protonation reaction.[16]

The $^{13}C\{^1H\}$ NMR spectrum (Figure 12a) also indicates the successful synthesis of the desired **75c**. The decreased coupling constant (relative to **74c**, $^2J_{PC}$ = 20.1 Hz) of the characteristic low-field doublet signal in this spectrum at δ 341.4 ppm ($^2J_{PC}$ = 18.2 Hz) is highly indicative of the decreased interaction between the P atom of PPh$_3$ and C_α which would accompany oxidation at the Ru atom. The general downfield shifting of the Tp-ligand signals relative to **74c** was also observed in this spectrum from δ 144.8-105.4 to δ 147.1-106.8 ppm.

Consideration of the $^{31}P\{^1H\}$ VT NMR spectra obtained from this reaction revealed much about the inherent instability of **75c**. For instance, while the quantitative formation of this complex is observed at -70 °C, some decomposition (~2% based on $^{31}P\{^1H\}$ NMR spectrum integrations) had taken place by the time a temperature of -60 °C had been achieved. This decomposition continued to accelerate until at 0 °C the complete

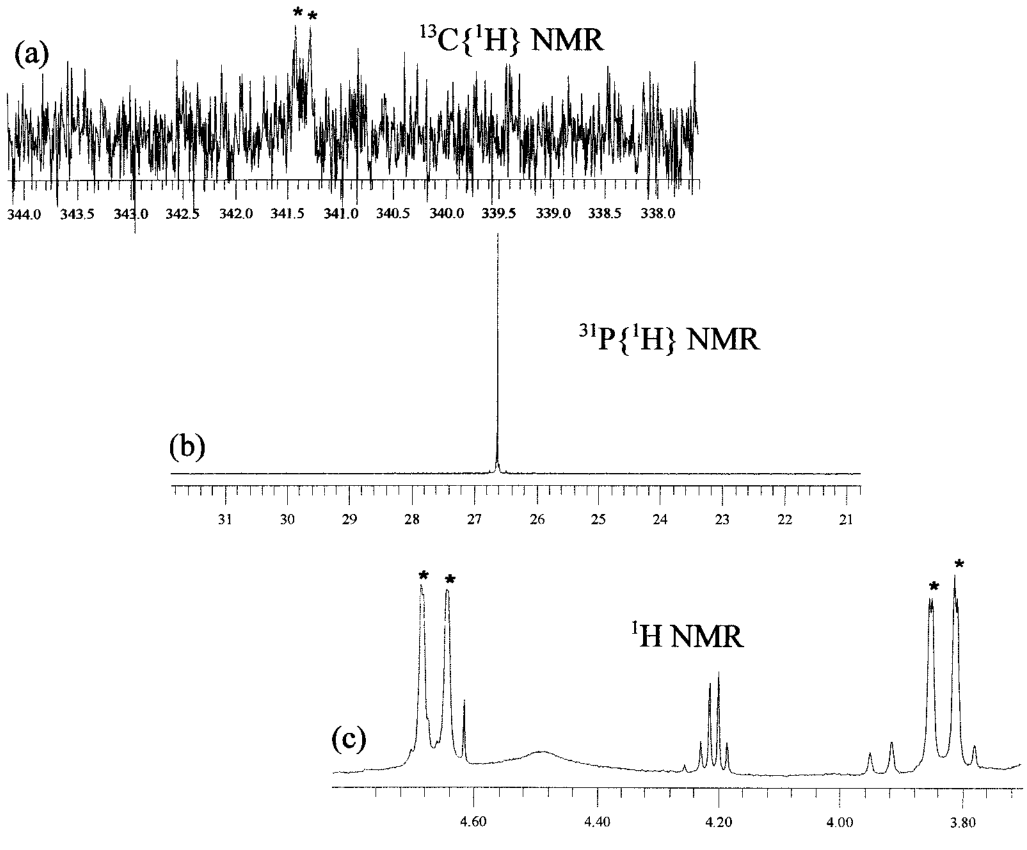


Figure 12: Low-Temperature (−70 °C) NMR Spectra of 75c in CD_2Cl_2 (selected regions).

Note: "*" indicates product peaks.

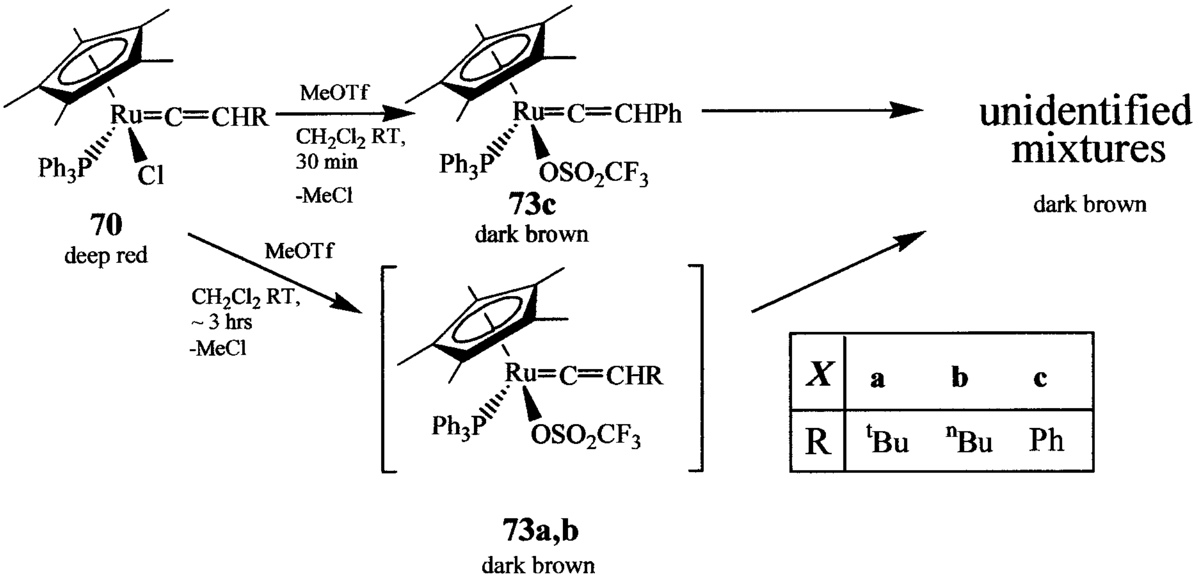
conversion of **75c** into a number of unidentified species was observed after 1 hr under these conditions. This behaviour follows very closely to that of the Cp* analogue **71c**, which also decomposes rapidly under similar conditions (see Section 4.1.5). Once again, the instability of this complex precluded its use in subsequent studies.

4.2 Methylation Reactions of Cp*RuCl(=C=CHR)(PPh$_3$) and TpRuCl(=C=CHR)(PPh$_3$) Complexes

In an attempt to broaden the range of electrophiles which might add to Ru-vinylidenes, electrophilic addition reactions involving Me$^+$ were also investigated with either of the Cp* and Tp series of complexes. Although these reactions were in general less selective, the spectroscopic data obtained therefrom suggested a different reaction course than that observed in the protonation reactions. These reactions are illustrated in Schemes 51 and 52, and explained in detail, below.

4.2.1 *Attempted C_β-methylation of **70a**.*

Observed as the least selective reactions of this project, the electrophilic additions of Me$^+$ to C_β of the alkyl-substituted Cp*Ru-vinylidenes Cp*RuCl(=C=CH(R))(PPh$_3$) (R = ^{t}Bu, **70a**; ^{n}Bu, **70b**) were attempted. Thus, treatment of a concentrated sample of **70a** in an NMR tube with one molar equivalent of neat MeOTf at −70 °C was followed by gradual warming to room temperature. An immediate change in colour from deep red to dark brown was observed. The reaction progress was monitored using ^{31}P{^{1}H} NMR spectroscopy, which revealed the nearly complete consumption of starting material (δ 52.4 ppm) within 3 hrs. and the appearance of a large number of other signals that could not be confidently assigned. Changing the reaction conditions (*i.e.*, amount of MeOTf) had little effect on the overall outcome of the reaction. The ^{1}H NMR spectrum, while extremely cluttered, revealed one particularly interesting peak at δ 3.0 ppm corresponding to MeCl.[17] This suggests that chloride abstraction by the Me$^+$ is likely taking place as



X	**a**	**b**	**c**
R	^{t}Bu	^{n}Bu	Ph

Scheme 51

opposed to electrophilic attack at C_β, forming some coordinatively unsaturated species. However, since the triflate ion is known to coordinate weakly to 16-e^- Ru in a few cases,[18] it is not unreasonable to speculate that this may be occurring in some capacity with the potential coordinatively unsaturated species despite the lack of unambiguous data.

4.2.2 *Attempted C_β-methylation of **70b**.*

The attempted reaction of **70b** with equimolar MeOTf at −78 °C in CD_2Cl_2 in an NMR tube under N_2 with gradual warming to room temperature gave results similar to that of the **70a**/MeOTf reaction. The immediate change in colour from deep red to dark brown indicated that a reaction had rapidly taken place. $^{31}P\{^1H\}$ NMR analysis revealed complete consumption of **70b** within ~3 hrs. accompanied by the rapid formation of many unidentified species. As with **70a**, this rapid decomposition precluded attempts at improving the production of a single species (*i.e.*, adding more MeOTf, see Section 4.2.3). Once again, ^1H NMR analysis of the complex mixture revealed the production of MeCl, consistent with electrophilic attack at the chloride ligand.

4.2.3 *Ambient Temperature Observation of $Cp^*Ru(OTf)(=C=CHPh)(PPh_3)$, **73c**.*

As with **70a** and **70b**, the reaction of $Cp^*RuCl(=C=CH(Ph))(PPh_3)$, **70c**, with MeOTf was also investigated. In contrast to previous reactions, this process entailed the preparatory scale reaction of a CH_2Cl_2 solution of **70c** with three equivalents of MeOTf at room temperature under N_2 to give a brown product. The larger scale reaction was employed in order to clean up the product enough to obtain a sufficiently pure sample for elemental analysis, and was prompted by the relatively few side products of this methylation reaction (*i.e.*, compared to that of **70a** and **70b**). Similarly, the increased quantity of MeOTf, relative to that used for **70a** and **70b**, was utilized in order to further clean up the reaction by accelerating the formation of the slowly but steadily-decomposing product. Analysis of the brown solid obtained using NMR spectroscopy confirmed the production of the unexpected yet understandable product $[Cp^*Ru(OTf)(=C=CH(Ph))(PPh_3)]$, **73c**.

By monitoring the progress of a reaction mixture prepared in an NMR tube using $^{31}P\{^1H\}$ NMR spectroscopy, it is clear that the vinylidene starting material is completely consumed after only 30 min. of reaction time. ^1H NMR spectra of this monitored reaction reveal the production of equimolar MeCl which, as in previous reactions, suggests that chloride abstraction has taken place. Also observed is a singlet at δ 4.54 ppm and a doublet at δ 1.39 ppm ($^4J_{PH} = 2.0$ Hz), which correspond to the vinylidene proton and the methyl protons of the Cp^*-ligand, respectively, of **73c**.

In the $^{13}C\{^1H\}$ NMR spectrum of complex **73c**, there is observed a low-field doublet at δ 344.3 ppm ($^2J_{PC} = 22.1$ Hz) which corresponds to C_α of the vinylidene ligand. The similarity of this signal to that of **70c** underscores the similarity in the C_α chemical environments of the two vinylidene species, which increases the likelihood that the triflate ion is coordinated to the Ru atom (*i.e.*, coordinatively unsaturated or dimeric species formed via chloride abstraction would likely give a very different C_α signal relative to the parent vinylidene). The ^{19}F NMR spectrum also supports this coordination since the appearance of the singlet at δ −79.1 ppm differs significantly from that of unreacted MeOTf (δ −75.2 ppm, based on an authentic sample).

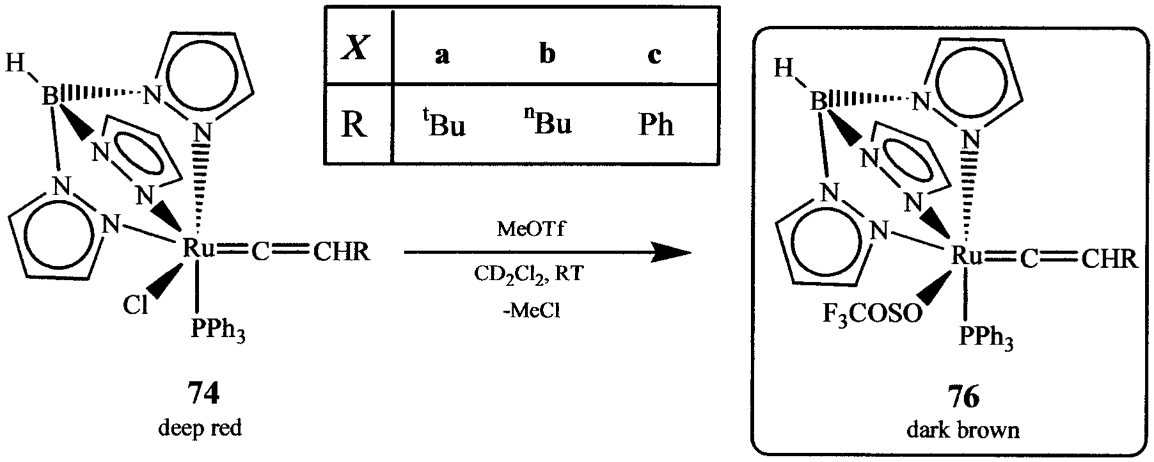
As in previous reactions (see Section 4.2.1), the probability that the triflate ion is coordinated to the Ru atom is strong.[18] For example, protonation of *cis-mer*-$RuH_2(CO)(Cyttp)$ with excess HOTf yields the di(triflato) complex *cis-mer*-$Ru(OTf)_2(CO)(Cyttp)$ with elimination of H_2.[18a] The elimination of H_2 also follows the treatment of CpRu(dfepe)H with HOTf to yield the triflato complex CpRu(dfepe)OTf.[18e] Similar treatment of $Cp^*Ru(NO)R_2$ (R = Me, Ph, *p*-tolyl) with HOTf results in elimination of RH and production of the triflato complex $Cp^*Ru(NO)(R)(OTf)$.[18c] Unfortunately, this proposed structure cannot be verified by X-ray crystal structure, which is unattainable due to the rapid (hours) decomposition of **73c** into several unidentified species in solution, even at low temperatures.

4.2.4 *Ambient-Temperature Observation of [TpRu(OTf)(=C=CH(^{t}Bu))(PPh$_3$)],* ***76a.***

Electrophilic addition reactions involving Me$^+$ were also extended to include the TpRu-vinylidenes TpRuCl(=C=CHR)(PPh$_3$) (R = ^{t}Bu, **74a**; ^{n}Bu, **74b**; Ph, **74c**) (Scheme 52). Similar results were observed in all cases (*i.e.*, elimination of MeCl). Although the products of these reactions also proved unstable, the reactions generally were more selective than those observed for the Cp*-analogues.

Methylation of **74a** was therefore investigated with the preparation of a sample of **74a** in an NMR tube in CD_2Cl_2 under N_2 followed by treatment with three molar equivalents of neat MeOTf at −78 °C. Gradual warming to room temperature was accompanied by an colour change to orange-brown. $^{31}P\{^1H\}$ NMR analysis indicated that the product **76a** is very unstable at room temperature. The greatest concentration of this product in the reaction mixture occurs after 15 min. of reaction at room temperature, with the mixture consisting of ~49% **76a** (δ 37.7 ppm) and ~40% **74a** (δ 40.4 ppm), based on $^{31}P\{^1H\}$ NMR spectrum integrations, along with several unidentified species. Reaction times longer than 15 min. resulted in the decomposition of **76a**. Three molar equivalents of MeOTf were necessary for observation of this product as the majority species. Therefore, after this period of reaction had been attained, the progress was frozen by rapidly cooling the sample tube to −40 °C. Immediate acquisition of spectral data via VT NMR spectroscopy was carried out following insertion of the sample tube into a precooled (−31 °C) NMR probe.

Analysis of the obtained ^{1}H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of the crude sample reveals that, as with **70a-c**, a chloride abstraction process had occurred as opposed to a methylation at C_β of the vinylidene. Most indicative of this is the downfield doublet present in the $^{13}C\{^1H\}$ NMR spectrum at δ 373.1 ppm ($^2J_{PC}$ = 16.3 Hz), a signal which is very dissimilar to that of the Ru-alkylidyne **75a**. Also derived from this spectrum is the observation that there is no downfield shifting of the Tp-ligand signals relative to those of **74a**, thereby refuting any speculation that an oxidation process at the Ru atom may have occurred.



X	a	b	c
R	^{t}Bu	^{n}Bu	Ph

74
deep red

76
dark brown

Scheme 52

Consideration of the ^{1}H NMR spectral data also supports the proposed identity of **76a** in this reaction. Firstly, the immediate appearance of a singlet at δ 3.02 ppm indicates the presence of MeCl generated in equimolar amounts based on relative integrations with other product peaks. This is consistent with chloride abstraction. The absence of any signals corresponding to the C_β-methylene hydrogen atom and the β-methyl group protons of an alkylidyne complex [TpRuCl(≡C–CH(Me)(^{t}Bu))(PPh$_3$)][OTf] indirectly supports this hypothesis. Furthermore, the doublet signal corresponding to the vinylidene proton of **76a** is also present at δ 4.27 ppm ($^4J_{PH}$ = 3 Hz), a shift similar to that of **74a** (δ 3.89 ppm, $^4J_{PH}$ = 3.8 Hz). Finally, no downfield shifting was observed to occur with the signals corresponding to the protons of the Tp-ligand.

Similar to data obtained for **73c**, a singlet in the ^{19}F{^{1}H} NMR spectrum at δ –79.5 ppm also suggests coordination of the triflate ion to the Ru atom.[18] Thus, all of the above spectral features are consistent with the abstraction of a chloride from the vinylidene starting material **74a**, resulting in the formation of the triflato complex [TpRu(OTf)(=C=CH(^{t}Bu))(PPh$_3$)] **76a**.

In terms of stability, small amounts (~10% from ^{31}P{^{1}H} NMR spectrum integrations) of **76a** may be observed in solution up to 24 hrs. after the addition of MeOTf. Unfortunately, the decomposition of this complex, as with **73c**, proved to be rapid and incessant upon initial formation based on monitoring by ^{31}P{^{1}H} NMR spectroscopy, yielding mixtures of unidentified species in the process.

4.2.5 *Ambient-Temperature Observation of [TpRu(OTf)(=C=CH(^{n}Bu))(PPh$_3$)],* ***76b.***

Much more exclusive and straight forward than the methylation of **74a** was that of **74b**. Thus, a sample of **74b** in an NMR tube under N$_2$ dissolved in CD$_2$Cl$_2$ was treated with three molar equivalents of neat MeOTf at –78 °C. The use of excess MeOTf maximizes the concentration of the product. The gradual warming of the solution to room temperature gave rise to a colour change from deep red to orange-brown. This was followed by immediate acquisition of NMR data at this temperature.

As was revealed by NMR data, a reaction pathway similar to that of the methylation reaction of **74a** had been adopted by this system, albeit to a greater degree. For instance, the close monitoring of reaction progress using $^{31}P\{^1H\}$ NMR spectroscopy reveals that there is a 69% presence (based on integration) of a species appearing at δ 39.0 ppm after 15 min. of reaction at room temperature. The ^1H NMR spectrum of the reaction mixture at this time period strongly supports the occurrence of halide abstraction by the methyl cation by displaying a peak at δ 3.03 ppm which integrates to one molar equivalent relative to the other product peaks of the spectrum. The multiplet signal (td, $^4J_{PH}$ =3 Hz, $^3J_{HH}$ = 8.4 Hz) corresponding to the hydrogen atom of the vinylidene ligand was also present in this spectrum at δ 4.35 ppm, which is at a slightly different position than that of **74b** (δ 4.05 ppm). Also, no significant change in chemical shifts of the signals for the protons of the Tp-ligand was observed.

Analysis of the reaction mixture using $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectroscopy also yielded data consistent with the production of $[TpRu(OTf)(=C=CH(^nBu))(PPh_3)]$, **76b**. From the $^{13}C\{^1H\}$ NMR spectrum, there is observed a low-field doublet signal at δ 369.8 ppm ($^2J_{PC}$ = 16.3 Hz) which is very similar to the chemical shift of the vinylidene complex **74b** δ 362.3 ppm ($^2J_{PC}$ = 19.2 Hz). There was also no observed downfield shifting of the signals corresponding to the Tp-ligand C atoms, which further supports the absence of any oxidation process. The observation of a singlet in the $^{19}F\{^1H\}$ NMR spectrum at δ −79.1 ppm also suggests coordinated triflate ion, as seen with other reactions of this type in this project (see Sections 4.2.3 and 4.2.4).[18] Taken together, this spectroscopic data suggests the formation of the triflato complex $[TpRu(OTf)(=C=CH(^nBu))(PPh_3)]$, **76b**. The decomposition of **76b** was observed to proceed immediately upon formation and is faster than that observed for **76a**. As an illustration of this rapid decomposition, there was no **76b** observed in a sample in an NMR tube after 24 hrs. of sample tumbling, which yielded a variety of decomposition products, as revealed by $^{31}P\{^1H\}$ NMR spectroscopy.

4.2.6 *Ambient-Temperature Observation of [TpRu(OTf)(=C=CH(Ph))(PPh_3)]*, **76c**.

The most selective methylation reaction which was observed to occur with a TpRu-vinylidene complex was that of [TpRu(OTf)(=C=CH(Ph))(PPh_3)], **74c**. Once a sample of **74c**, under N_2, in an NMR tube was dissolved in CD_2Cl_2, the addition of three molar equivalents of neat MeOTf was effected via syringe at −78 °C. A colour change from deep red to orange-brown was observed. Gradual warming of the sample to room temperature was followed by acquisition of NMR data using a room temperature NMR probe.

The majority presence of product species **76c**, appearing at δ 37.4 ppm in the $^{31}P\{^1H\}$ NMR spectra (~89% based on $^{31}P\{^1H\}$ NMR spectrum integrations), was observed after 90 min. of reaction. This species persists well past 30 hrs. at room temperature, at which point the product peak integrates at 50%.

Support for the failure of the C_β-methylation reaction was found upon consideration of the ^1H NMR spectrum. As with the other methylation reaction explored during this project, a signal in this spectrum at δ 3.02 ppm corresponding to MeCl was observed. A doublet signal at δ 5.40 ppm ($^4J_{PH}$ =3.5 Hz) corresponding to the vinylidene hydrogen resembles that of **74c** at δ 4.92 ppm ($^4J_{PH}$ =3.8 Hz). Once again, the signals of the Tp-ligand hydrogens had not undergone a change in chemical shift toward lower field which supports the absence of any oxidation process.

Similar results are obtained from the $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra. The appearance of a low-field doublet at δ 377.4 ppm ($^2J_{PC}$ = 17.3 Hz) suggests a similarity between the product species and the parent vinylidene **74c**, which exhibits a doublet at δ 368.0 ppm ($^2J_{PC}$ = 20.1 Hz). There was also no observed downfield shifting of the signals corresponding to the Tp-ligand C atoms, which is consistent with no change in the formal oxidation state of the Ru-centre. Finally, the observation of a singlet in the $^{19}F\{^1H\}$ NMR spectrum at δ −78.9 ppm strongly suggests that the triflate ion is coordinated to the Ru atom in the product of this reaction, as seen with other methylation reactions in this project.[18] This spectroscopic data supports the formation of

[TpRu(OTf)(=C=CH(Ph))(PPh$_3$)], **76c**.

4.3 Chemistry of Cp*RuCl(=C=CHR)(PPh$_3$) versus TpRuCl(=C=CHR)(PPh$_3$) Complexes

As mentioned in the introductory paragraph of the Results and Discussion section, the comparison of the Cp* and Tp ligands by Bergmann et al.[5] serves to rationalize the comparison of the reactivity of Cp*- and Tp-substituted Ru-vinylidene complexes toward the electrophiles H$^+$ and Me$^+$. While sufficient data to explain exhaustively any similarities or differences observed in this reactivity has not been collected during the course of this project, adequate results were obtained to at least speculate on these comparisons as they pertain to the relative steric and electronic properties of these two ligands. A summary of the spectroscopic data acquired during this project is presented in Table 7.

The first comparison involves the observed decreases (*i.e.*, relative to the parent vinylidenes) in the $^2J_{PC}(C_\alpha)$-value of the low-field doublet present in the $^{13}C\{^1H\}$ NMR spectrum of every alkylidyne complex produced during this project. This ubiquitous change in the interaction between the P atom of PPh$_3$ and C_α is of a different magnitude for each complex, an observation which may allow some speculation as to the relative importance of steric and electronic factors in this change.

Another interesting comparison of spectral data may be made between the magnitude of change in the $^2J_{PC}(C_\alpha)$-values upon protonation of the vinylidene starting materials of the two classes of complexes. In the case of complexes **71a-c**, this change is rather large at 7-8 Hz. By comparison, the corresponding change in the $^2J_{PC}(C_\alpha)$-values of complexes **75a-c** is much less pronounced at 2-3 Hz (Table 7). Recognition of this dissimilarity in spectral data trends is important since it clearly illustrates that identical oxidation processes imposed upon these two types of complexes effect different changes in the spectral properties of the complexes in question.

Table 7: Summary of NMR Spectroscopic Data for Complexes 70-76 (Selected Signals)

Complex	$\delta(C_\alpha)$ (ppm)	$^2J_{PC}(C_\alpha)$ (Hz)	$\delta(Cp^*)$ (ppm)	$\delta(Tp)$ (ppm)
70a	336.5	23.6	1.41	N/A
70b	334.7	24.4	1.45	N/A
70c	340.1	24.4	1.48	N/A
71a	351.0	15.7	1.65	N/A
71b	349.4	17.1	1.56	N/A
71c	340.6	16.3	1.60	N/A
72a	348.3	15.7	1.61	N/A
72b	347.0	17.1	1.56	N/A
73c	344.3	22.1	1.39	N/A
74a	365.1	19.2	N/A	8.10-5.73
74b	362.3	19.2	N/A	8.22-5.71
74c	368.0	20.1	N/A	7.88-5.75
75a	355.2	16.5	N/A	7.97-5.97
75b	351.2	17.5	N/A	7.89-5.99
75c	341.4	18.2	N/A	7.81-5.93
76a	373.1	16.3	N/A	7.88-5.74
76b	369.8	16.3	N/A	8.23-5.72
76c	377.4	17.3	N/A	8.38-5.75

Complex Legend:

70a-c → $[Cp^*RuCl(=C=CHR)(PPh_3)]$

71a-c → $[Cp^*RuCl(\equiv C-CH_2(R))(PPh_3)][BF_4]$

72a,b → $[Cp^*RuCl(\equiv C-CH_2(R))(PPh_3)][B(Ar^f)_4]$

73c → $[Cp^*Ru(OTf)(=C=CH(R))(PPh_3)]$

74a-c → $[TpRuCl(=C=CHR)(PPh_3)]$

75a-c → $[TpRuCl(\equiv C-CH_2(R))(PPh_3)][BF_4]$

76a-c → $[TpRu(OTf)(=C=CH(R))(PPh_3)]$

This observation is not surprising since the literature values for the cone angles of the Cp* and Tp ligands, at 182° and 262°,[4] respectively, underscores the fact that the octahedrally-forcing Tp ligand system possesses such steric bulk that the oxidation of the Ru atom may not additionally effect the interaction between the P atom of PPh_3 and C_α to the same extent as in the case of the Cp*-complexes. This speculation is also reflected in the lower $^2J_{PC}(C_\alpha)$-values of the TpRu-vinylidenes **74a-c** relative to **70a-c** (see Table 7). In terms of electronic considerations, it is also possible to speculate that the increased electron-donation by Cp* relative to Tp may increase the amount of backdonation by Ru to the π-acidic vinylidene ligand, thereby resulting in a shorter Ru=C bond and a higher $^2J_{PC}(C_\alpha)$-value for complexes containing the former ligand. Comparative studies involving the measured ν(CO) values for analogous Cp*Ru-carbonyl and TpRu-carbonyl complexes have shown that increased backdonation to the π-acidic CO ligand is generally observed with complexes containing the former ligand (*i.e.*, lower ν(CO)) as opposed to the latter (*i.e.*, higher ν(CO)).[5]

Another comparison which may be drawn between complexes **71a-c** and **75a-c** involves the observed stabilities of these alkylidyne species. As outlined in Section 4.1 above, there is no question that the Cp*Ru-alkylidynes **71a-c** are much more stable than their TpRu-analogues **75a-c**. This may be understood upon consideration of the relative electron-donating properties of these ligands. The stronger electron-donation by the Cp* ligand relative to the Tp ligand (*i.e.*, with Ru and Os)[5] appears to stabilize Ru^{IV} produced upon protonation of the parent vinylidenes. There may also be comparisons made between relative alkylidyne stabilities within each group, a characteristic which is highly dependent on the identity of the alkylidyne substituent. It is observed in both groups that the stability of the complexes varies with the alkylidyne substituents in the order Ph $\langle$ ^{n}Bu $\langle$ ^{t}Bu. Since this trend is identical to that of the Lewis basicity of these functional groups,[7] it may be concluded that the stability of the alkylidyne complexes in this project is directly dependant on the basicity of the alkyidyne substituent.

Both groups of vinylidenes are also observed to adhere to the same reaction courses when reacting with the electrophiles H^+ and Me^+. For instance, treatment of the parent vinylidenes with $HBF_4 \bullet Et_2O$ results in the electrophilic addition of H^+ to C_β to form the alkylidyne product in every case. However, as described in Section 4.2, the attack of the vinylidene C_β by Me^+ is not observed to be the reaction course for any of the parent vinylidenes. Observed instead is the abstraction of the chloride ligand to form MeCl. One possible reason for this is that the steric crowding around Ru by the enormous Cp^*/Tp and PPh_3[8] ligands likely inhibits attack at C_β by Me^+, an issue which apparently does not prevent attack here by H^+.

In terms of the mechanism of this chloride abstraction, it is unknown whether attack of the chloride by Me^+ occurs directly or through some intermediate species formed through attack at other sites on the molecule (*i.e.*, metal or vinylidene ligand). In either situation, the Me^+ would be able to reductively eliminate with the chloride to form MeCl and a coordinatively unsaturated species (migration of the Me^+ to the metal atom would be required after attack at the vinylidene ligand in order to facilitate reductive elimination of MeCl). Attack at a metal-vinylidene C_β by Me^+ has been previously reported by Templeton et al. using a W-vinylidene.[19] Therefore, this feasiblely could be the case with this system, were it not for the absence of the corresponding intermediate $[(L)RuCl(\equiv C-CH(Me)R)(PPh_3)][OTf]$ ($L = Cp^*$, Tp; $R = {}^tBu$, ${}^nBu$, Ph) in acquired NMR spectra.

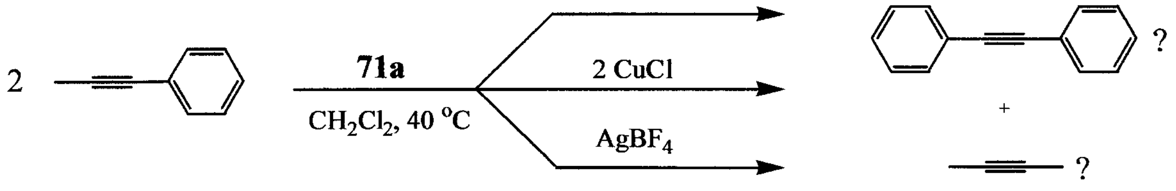
Furthermore, it is generally accepted that halide abstractions carried out by nonmetal electrophiles involve the direct attack of the halide by the electrophile.[20] This is a much more probable mechanism since it entails attack by the Me^+ species at the more exposed lone pairs of the chloride ligand. Also, electrostatic repulsive forces likely exist between the filled d-orbitals on the Ru atom and these lone pairs on the chloride. This would serve to enhance the basicity of this ligand, as was shown previously by Caulton.[21] The abstraction mechanism probably involves the partial ionization of the chloride ligand in a type of S_N1 reaction, which is not entirely unexpected in a CH_2Cl_2 medium. The alternative concerted S_N2 pathway, which would involve the formation of a chloromethane complex, is also possible. The main conflict with the latter mechanism is that while iodomethane complexes of Ru have been reported,[17] the stability of these complexes are likely dependant on the softness of the I atom's Lewis basicity. The relatively hard Lewis basicity of the chloride ligand would therefore likely discourage this pathway, or perhaps inhibit it to below the threshold of detection by NMR spectroscopy.

The short-lived presence of a potential chloromethane complex is also foreshadowed by the observed lability of CH_2Cl_2 in η-CH_2Cl_2 complexes of transition metals. For instance, the Ru-based $[Ru(H)(CO)(\eta^2\text{-}ClCH_2Cl)(P^tBu_2Me)_2][BAr^f_4]$[22] has exhibited a high CH_2Cl_2-lability towards displacement by the weakly-coordinating species Et_2O.[23] The CH_2Cl_2 ligand of Pt-based species *trans*-$[Pt(H)(\eta^1\text{-}ClCH_2Cl)(P^iPr_3)_2][BAr^f_4]$ is also susceptible to substitution by such weakly-coordinating ligands as PhX.[24] The complex $[Cp^* Ir(\eta^1\text{-}CH_2Cl_2)(PMe_3)(Me)][BAr^f_4]$ is not only vulnerable to CH_2Cl_2-substitution by such ligands as CO, MeCN, and Et_2O, but also by the oxidative addition of C−H bonds of alkane species.[25]

4.4 Attempted Application of **71a** in Alkyne Cross Metathesis of MeC≡CPh

Once the successful synthesis of new Ru-alkylidyne complexes was confirmed, efforts were made to explore the reactivity of this class of compounds towards the metathesis of alkyne substrates. The alkyne compound MeC≡CPh was chosen as the test substrate for these studies since the alkyne cross metathesis of 2-propynyl species with themselves results in the production of the volatile byproduct MeC≡CMe, which may be efficiently removed from the reaction mixture.[26] The alternative volatile-producing substrate HC≡CPh was not considered for this purpose for fear that its acidic acetylenic hydrogen atom[27] might interfere with the desired reaction pathway.

The only sufficiently stable alkylidyne species synthesized during this project, $[Cp^*RuCl(\equiv C{-}CH_2(^tBu))(PPh_3)][BF_4]$, **71a**, was dissolved in CH_2Cl_2 and treated with 20 molar equivalents of MeC≡CPh in an attempt to effect alkyne cross metathesis (Scheme 53).



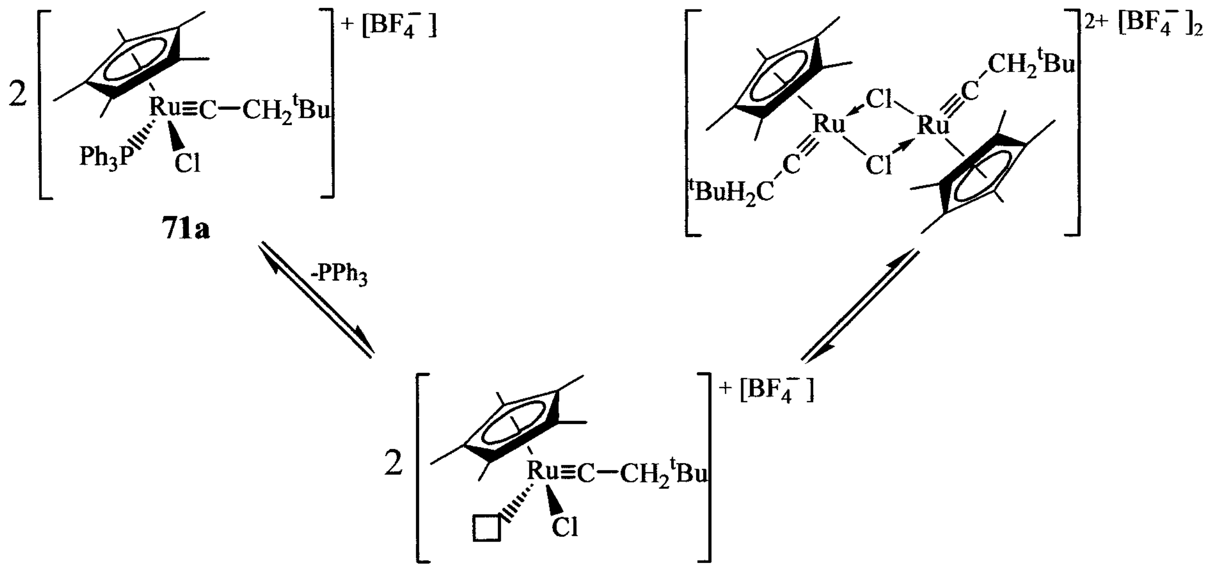
Scheme 53

The reactions made use of the dynamic vacuum technique and high reaction temperatures (40 °C) in an attempt to remove any MeC≡CMe produced, thereby driving the metathesis process forward. The solvent-removed residues of the reaction mixtures were extracted with Et_2O in order to collect the supposed product PhC≡CPh. Subsequent removal of Et_2O with analysis of the residues by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy identified MeC≡CPh as the sole organic constituent based on comparison with spectra obtained from an authentic sample. The analysis of the remaining residue (*i.e.*, Et_2O-insoluble catalyst portion) using $^{31}P\{^1H\}$ NMR spectroscopy revealed that decomposition of **71a** had not taken place.

After these initial attempts failed, efforts were made to facilitate the activation of the precatalyst species **71a** toward effective metathesis. Since phosphine dissociation was found by Grubbs et al. to be crucial to metathesis of olefins by Ru-alkylidenes,[28] the same speculation can be made in the context of this experiment. The first such endeavour utilized two molar equivalents of CuCl as a scavenger of any phosphine which may dissociate from the precatalyst **71a** during the metathesis process. Once again the analysis of the products of this reaction revealed that only MeC≡CPh was present as an organic constituent and that the integrity of the **71a** was preserved (*i.e.*, no decomposition as indicated by analysis of the catalyst residue using $^{31}P\{^1H\}$ NMR spectroscopy).

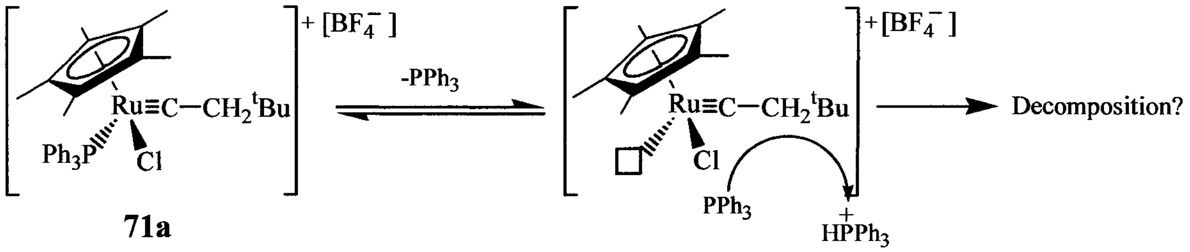
Having failed at enhancing some metathesis-friendly phosphine dissociation process, attention was turned toward forcible generation of a vacant coordination site on the metal. The facilitation of metathesis via abstraction of a chloride ligand from **71a** was therefore attempted through the use of equimolar $AgBF_4$ under light-protected conditions. A colour change from orange to green was observed after ~30 min. of reaction. Despite the ~70% decomposition of **71a** into many unidentified species during the reaction (based on the integration of the $^{31}P\{^1H\}$ NMR spectrum of the Et_2O-washed catalyst residue), the analysis of the residue obtained from the Et_2O-extraction identified only MeC≡CPh as an organic constituent.

The failure of **71a** to effect metathesis of alkyne substrates may be based on the extreme steric crowding around the Ru atom by the large Cp^* and PPh_3, as well as by the bulky ^tBu-substituent on the alkylidyne ligand. This speculation is supported by the absence of alkyne metathesis in the presence of $AgBF_4$ even though substantial decomposition of **71a** is observed under these conditions. Dissociation of a phosphine ligand from **71a** may also require higher reaction temperatures in order to be sufficiently prolific for alkyne metathesis to occur, and may be frustrated by the fact that the parent alkylidyne is cationic. A possible modification of this complex through the substitution of PPh_3 with a bulkier phosphine ligand, such as PCy_3, may increase the likelihood of phosphine dissociation, although it is unknown how this would affect the stability of the resultant complex. Another possible deterrent of metathesis processes is the possible dimerization of the coordinatively unsaturated complex fragments formed upon phosphine dissociation from **71a**, thereby deactivating the catalyst species (Scheme 54).



Scheme 54

Although this type of dimerization has been previously observed with a coordinatively unsaturated Ru-allenylidene (see Section 1.2.2.6), the steric interactions between the bulky ancillary ligands on each fragment may not favour dimerization in this case. Deactivation of the catalyst species could also be caused by the deprotonation of the alkylidyne ligand by free phosphine in the reaction mixture (*i.e.*, formed upon dissociation from **71a**), forming the corresponding vinylidene species which likely would not possess alkyne metathesis activity (Scheme 55).



Scheme 55

This decomposition would likely be potentiated at higher reaction temperatures.

These results serve as good indicators that the use of this Ru-alkylidyne in alkyne metatheses may not necessarily be applicable to cross metathesis. Further work with this class of complexes will no doubt yield a more complete picture of the behaviour of these complexes toward metathesis processes.

4.5 Results and Discussion References

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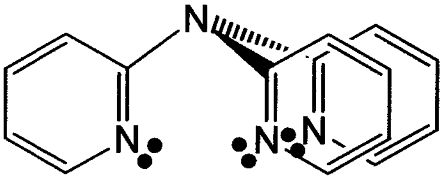
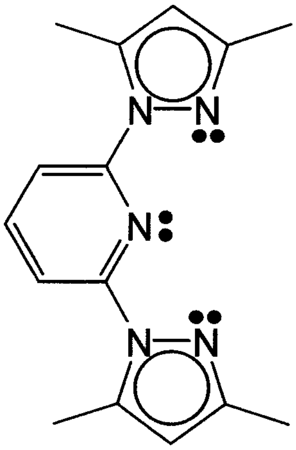
5. Suggestions for Further Work

The results obtained during this project indicate that the preparation of several new Ru-alkylidynes has been successfully achieved via electrophilic addition of H^+ to C_β of various vinylidene starting materials. In the area of Ru-alkylidynes, the following pursuits would likely serve to provide some valuable insight into these complexes and their potential utility in alkyne cross metathesis:

(1) The use of the bulky ancillary ligands Cp* and Tp has proven to be an effective strategy for the production of Ru-alkylidynes with moderate-to-excellent stability. How would this stability change if one were to utilize other polydentate ligands, such as tri-2-pyridylamine (TRIPYAM) or 2,6-(3,5-dimethyl-*N*-pyrazolyl)pyridine (Me_4BPP), in the synthesis of Ru-alkylidynes?



Tri-2-pyridylamine (TRIPYAM)



2,6-(3,5-dimethyl-N-pyrazolyl)pyridine (Me_4BPP)

(2) The activity of **71a** towards alkyne cross metathesis was not observed to be significant under the conditions used in those experiments. Would employment of more rigorous reaction conditions, such as higher temperatures (*e.g.*, boiling benzene) and longer

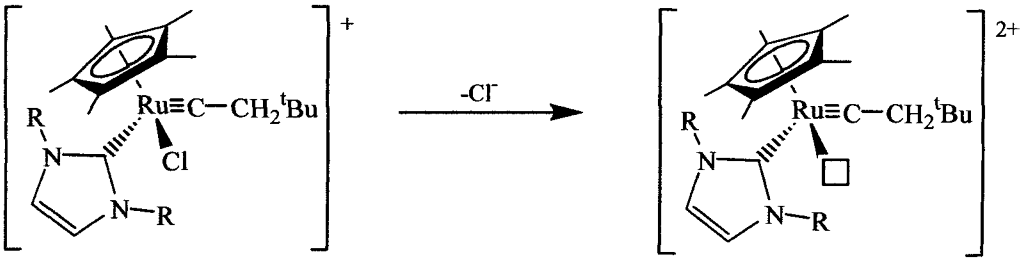
reaction times, affect this activity? Furthermore, how would the metathesis activity of **71a** be affected if one of the above ligands were used in place of Cp^* in the preparation of Ru-alkylidynes?

(3) When adding CuCl, a phosphine scavenger, to the metathesis reaction mixture, no wide scale decomposition of **71a** was observed, suggesting that phosphine dissociation does not readily occur with this complex under the conditions used in those experiments. What would be the effect on metathesis activity and complex stability of **71a** if PPh_3 were replaced by a bulkier phosphine ligand, such as PCy_3? Assuming a sufficiently stable Ru-alkylidyne was obtained, would higher reaction temperatures significantly enhance metathesis activity, or would they accomplish more in the way of catalyst decomposition?

(4) When $AgBF_4$ was added to the metathesis reaction mixture of **71a**, substantial decomposition of this complex was observed, albeit with no increase in metathesis activity. Into what species did **71a** decompose? Can any of them be isolated, and if so, how may they direct future Ru-alkylidyne synthetic efforts and metathesis applications? Also, assuming that the expected chloride abstraction process was the principle decomposition mechanism of **71a** under these conditions, why could the alkyne substrate not coordinate to the vacant site generated on the metal? Was it because of the steric crowding of the metal by the ancillary ligands? If so, could utilization of a less bulky phosphine ligand, such as PMe_3 or $P(^{n/i}Pr)_3$, in conjuction with $AgBF_4$ provide an alkyne-metathesis-active Ru-alkylidyne system? Was substrate concentration a factor? Perhaps use of more concentrated reaction mixtures would serve to increase the likelihood of alkyne coordination before decomposition of the catalyst species (*i.e.*, assuming chloride abstraction). Furthermore, could the lifetime of the coordinatively unsaturated Ru^{IV} centre produced after chloride abstraction from **71a** be extended through the use of more Lewis basic (trialkyl)phosphines (*i.e.*, compared to PPh_3) in preparation of the catalyst complex?

(5) How would MeOTf act as a chloride abstracting agent for the alkylidyne complex **71a**? Would there be competition between sites of attack (*i.e.*, chloride *vs.* hydrogens on C_β), or would the steric bulk of the ancillary ligands direct the methylation process toward the chloride ligand, as was observed with every (chloro)vinylidene complex studied during this project (Section 4.2)? If so, would the lifetime of the resulting dicationic alkylidyne species be long enough for significant alkyne metathesis to occur?

(6) To solve the issue concerning the deprotonation of the alkylidyne ligand by dissociated phosphine, the use of an N-heterocyclic carbene (*i.e.*, NHC) ligand in place of a phosphine ligand is one possibility (see Section 1.2.2.2). In that case, abstraction of the chloride ligand by $AgBF_4$ would generate a complex fragment that would still find stabilization for its Ru^{IV} centre from the generous donation of electron density by the NHC ligand. Furthermore, the stronger σ-donation of NHC ligands compared to phosphine ligands results in a stronger covalent bond between this ligand and the Ru atom, thereby preventing dissociation of this ligand and subsequent deprotonation of the alkylidyne species (Scheme 56).



Scheme 56

The electrophilic addition of Me^+ to the vinylidene C_β was not observed to occur with any of the vinylidenes studied in this project. Since this has previously been reported to occur with a W-vinylidene complex (Section 4.3), it is reasonable to assume that the same should be possible with vinylidene complexes of other metals. The following investigations may help provide the first occurrence of this with a Ru-vinylidene:

(1) The reaction of MeOTf with the vinylidenes in this project resulted in the abstraction of the more vulnerable chloride ligand (*i.e.*, compared to C_β) to form MeCl in every case. Since steric crowding around C_β is likely a strongly-contributing factor to this selectivity, could the use of less bulky ancillary ligands enhance the accessibility of C_β toward attack by Me^+?

(2) Since chloride abstraction is observed to be the main reactive pathway, would bis(phosphine)-Cp^*/TpRu-vinylidene complexes have better success of Me^+-addition to the vinylidene C_β? How stable would any resultant Ru-alkylidynes be (*i.e.*, protonation reactions generally more reversible than methylation reactions)? Since a few dicationic Ru-alkylidynes are already known (Sections 1.4.2.4, 1.4.2.6, and 1.4.2.7), how could these influence the production of new Ru-alkylidynes via this method (*i.e.*, choices in ancillary ligands)?

(3) The Ru-triflato(vinylidenes) prepared during this project were generally unstable, most decomposing within a day in solution. Into what did they decompose? Can these species be isolated, and if so, what can they tell us about the reactivity of this relatively small class of vinylidene compounds? How can this knowledge be used to generate new vinylidene compounds, and will there be any applicability to Ru-alkylidynes?